HELSINKI UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry and Materials Sciences
Degree Programme of Forest Products Technology

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ALTERNATIVE APPLICATION TO FATTY ACID STRATEGY IN DEINKING

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 13 November, 2008.

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ABSTRACT OF MASTER'S THESIS

Author

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Title of Thesis

Alternative Application to Fatty Acid Strategy in Deinking

Abstract

The objective of this thesis was to test chemicals that could be used in deinking instead of fatty acid based soap. The non fatty acid based chemicals tested were based on silicone derivatives. The driving forces behind finding other options for fatty acid are the increasing prices of chemicals and energy. Energy is required for storing of fatty acid soaps; to prevent fatty acid solidifying it has to be stored at a temperature of at least 70 °C.

In the theory part the basics of the whole deinking process was covered and the most used chemicals were studied in main points. Also the deinking process of the Stora Enso Sachsen GmbH mill was summarily reviewed and more attention was paid to the differences of the two types of flotation cells used at the mill.

The experimental part consists of two sections; laboratory studies and a mill scale trial run. In the laboratory the effect of different chemicals and varying dosage amounts on the deinking were tested: tests were made with a laboratory cell. The superiority of the chemicals was evaluated e.g. from the brightness measured and the losses of ash and total defined from the flotated pulp. One product was chosen to be tested in mill conditions. The product chosen was not the best according to the laboratory results but one of the newest on the market. The mill scale trial was made in collaboration with the supplier of the chosen chemical.

In the laboratory studies highest brightness was achieved with fatty acid based soaps. But when the increase of brightness and losses are considered silicone derivatives have potential. The values of reject amounts measured are controversial because in laboratory flotation the amount of reject can be easily influenced by using different methods to fill the cell.

In the mill scale trial soap was replaced with the new product progressively. The beginning of the trial proceeded well and the silicone derivative seemed to function. Problems arrived when soap was removed from secondary flotation, brightness collapsed and froth was too stable and caused overflow. Also the type of flotation cell played a role in how well the silicone derivative functions; with newer cell models the silicone derivative gave better results. According to this trial the fatty acid based soap will remain in the process at least for now.

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Alternative Application to Fatty Acid Strategy in Deinking

Tiivistelmä

Tämän työn tarkoituksena oli tutkia kemikaaleja, joita voitaisiin käyttää siistausprosessissa rasvahappopohjaisten kemikaalien sijaan. Testattavana olleet muut kuin rasvahappopohjaiset kemikaalit olivat silikonipohjaisia. Kasvavat energian ja kemikaalien hinnat houkuttelevat etsimään vaihtoehtoja rasvahappopohjaisille saippuoille, joiden varastoinnissa vaaditaan energiaa. Jotta rasvahappo pysyisi nestemäisenä, tulee sitä säilyttää yli 70 °C lämpötilassa.

Kirjallisuusosa kattaa perusteet koko siistausprosessista sekä pääkohdat tyypillisimmistä siistauskemikaaleista. Myös Stora Enso Sachsen GmbH:n siistauslaitoksen prosessi on kuvattu sekä hieman seikkaperäisemmät tiedot kahdesta tehtaalla käytettävästä siistauskennomallista.

Kokeellinen osuus koostuu kahdesta osasta, laboratorio kokeista ja tehdasmittakaavaisesta koeajosta. Laboratoriokennon avulla tutkittiin eri siistauskemikaaleja ja niiden eri annostusten vaikutusta siistauksen lopputulokseen. Kemikaalien paremmuus arvioitiin siistatusta sulpusta tehtyjen kokeiden avulla, kuten saavutetusta vaaleudesta sekä kuiva-ainepitoisuuden ja tuhkan häviönä. Kemikaali, joka valittiin tehdasmittakaavaiseen koeajoon, ei antanut laboratoriokokeissa parhaita tuloksia, mutta on yksi uusimmista markkinoilla olevista tuotteista. Koeajo tehtiin yhteistyössä kemikaalitoimittajan kanssa.

Laboratoriokokeissa korkeimmat vaaleudet saavutettiin rasvahappopohjaisilla saippuoilla, mutta tarkasteltaessa vaaleuden nousua sekä kuiva-ainepitoisuuden ja tuhkan häviöitä, on silikonipohjaisella siistauskemikaalilla potentiaalia. Tulokset rejektin määristä on kiistanalaisia, sillä rejektin määrään voidaan helposti vaikuttaa täyttämällä laboratoriokenno eri tavoin. Tehdasmittakaavaisessa koeajossa rasvahapposaippua korvattiin asteittain silikonipohjaisella siistauskemikaalilla. Aluksi koeajo sujui hyvin, ongelmia ilmeni vasta, kun saippua poistettiin sekundääriflotaatioista, vaaleus laski ja lietevaahto ei hajonnut, jolloin lietesäiliö tulvi yli. Huomattavissa oli myös, että erityyppisillä flotaatiokennoilla on vaikutusta silikonipohjaisen siistauskemikaalin toimintaan, uudemmalla tekniikalla saatiin parempia tuloksia. Tämän koeajon perusteella rasvahappopohjainen saippua on ainakin toistaiseksi käytössä siistausprosessissa.

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tl

Job description

by M.Sc. Franziska Schütt

The main purpose of deinking plants is the removal of ink from fibres. Therefore special chemicals like fatty acid are used. The prices for fatty acid based on animals are increasing dramatically since cadavers are also used for energy production. That was one reason for Stora Enso Sachsen GmbH to change to vegetable fatty acid in summer 2007. Main suppliers of fatty acid react on this development by creating new deinking chemicals. New products like silicone derivative are on the market and promise good performances in the deinking process. These products promise in addition to a good ink removal also a possibility to lower pH-value in the process. Lower pH will give the opportunity to lower usage of caustic and by that also decrease of peroxide due to lower yellowing effect. Positive secondary effects can be seen in the lower charge due to lower dosage of caustic and by that the possibility to decrease chemicals used in water cleaning process.

The production of fatty acid is a complex process which requires energy for heating. It is also not clear yet which administrative work is necessary if the production of soap has to be registered due to the new regulations of "REACH".

These are the main reasons for Stora Enso Sachsen GmbH to search for alternative application to the present fatty acid strategy. Target for the final thesis should be to test different products from different suppliers in lab scale and to find the best product for Stora Enso Sachsen GmbH. The main target is the proposal of a new product for a full scale trial with recommendation of dosing points and amounts, cost saving potential and evaluation of possible secondary effects.

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I would like to thank my parents for the support throughout my whole education career and I am grateful that they have endured the length of it with very little complaint. My brother and his family I wish to thank for being there when needed and giving me advice when asked.

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Otaniemi, Finland, 13.11.2008

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List of abbreviations

CEPI	Confederation of European Paper Industries
HC	High Consistency
MC	Medium Consistency
LC	Low Consistency
ONP	Old Newspaper
OMG	Old Magazine
DAF	Dissolved Air Flotation
SE	Stora Enso
IC	Intermediate Consistency
HLB	Hydrophilic-lipophilic Balance
EO/PO	Ethylene Oxygen/Propylene Oxygen
COD	Chemical Oxygen Demand
polyDADMAC	Polydiallylmethylammonium
FAS	Formamidine Sulfinic Acid
HW	Hyperwashing, Hyperwashed
IDM	Induktiver Durchflussmesser (on-line flow meter)
FS	Fine Screening
U.S.	United States

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1 INTRODUCTION

Recovered paper is nowadays an important raw material for papermaking, especially for the European paper industry. In Europe the main print products of recovered paper for deinking are newspapers and magazines /1/. Recovered paper is used e.g. to produce newsprint, board and tissue products. The consumption of recovered paper started to increase notably in the beginning of the 1980's and until the mid 1990's the increase was ca. 6 % annually /2/. After that the increase of consumption slowed down for a while but during the period 2000 - 2006 the annual increase was 4,5 % /3/. Globally in 2006 199 million tonnes of recovered paper was used of which 49 million tonnes was used in the CEPI (Confederation of European Paper Industries) member countries. China is also a significant user of recovered paper and almost half of the amount consumed there is imported, mostly from North America.

Lately prices in general have been soaring, and especially for energy and food. The increasing demand for energy and the rising price of oil has made biodiesel a more and more attractive option. The basic raw materials for biodiesel are fatty acids. Fatty acids are found in plants and animal fats, so that the energy industry competes with the food industry and prices rise. As fatty acids are also the raw material for soap used in flotation the production costs of deinked pulp increases. When also the increasing prices of recovered paper caused by expanding demand and the energy costs are considered, it is natural that interest lies in cutting production costs anywhere possible. All this challenges the industry to make the deinking process more cost effective while still maintaining good quality.

The purpose of this thesis was to study whether fatty acid soap as a collector in flotation deinking could be replaced with another product. A few possibilities were tested in laboratory scale trials and the results were compared to those gained with few different fatty acid based soaps. In the laboratory trials the focus was more towards silicone derivatives. Also a mill scale trial was made with one of the products based on silicone derivatives.

2 DEINKING PROCESS

2.1 General

In deinking the aim is to remove printing ink and other contaminants from recovered paper, preserve the original characteristics of fibres and get the brightness and the cleanliness of the deinked pulp as high as necessary. For removing the contaminants from recycled paper and to get clean and bright pulp mechanical forces, heat and different chemicals are used /4/. These energy inputs interact with each other helping the ink removal. The deinking process consists of several process stages but all available stages are not included in all systems /5/. All stages can have a number of sub processes to make the whole process even more complex. The process varies with raw material and location. A simple example of the deinking process is presented as a flowchart in figure 1. As can be seen there are lot of phases where the pulp is thickened and diluted again. Pulp is always diluted for flotation and thickened afterwards.

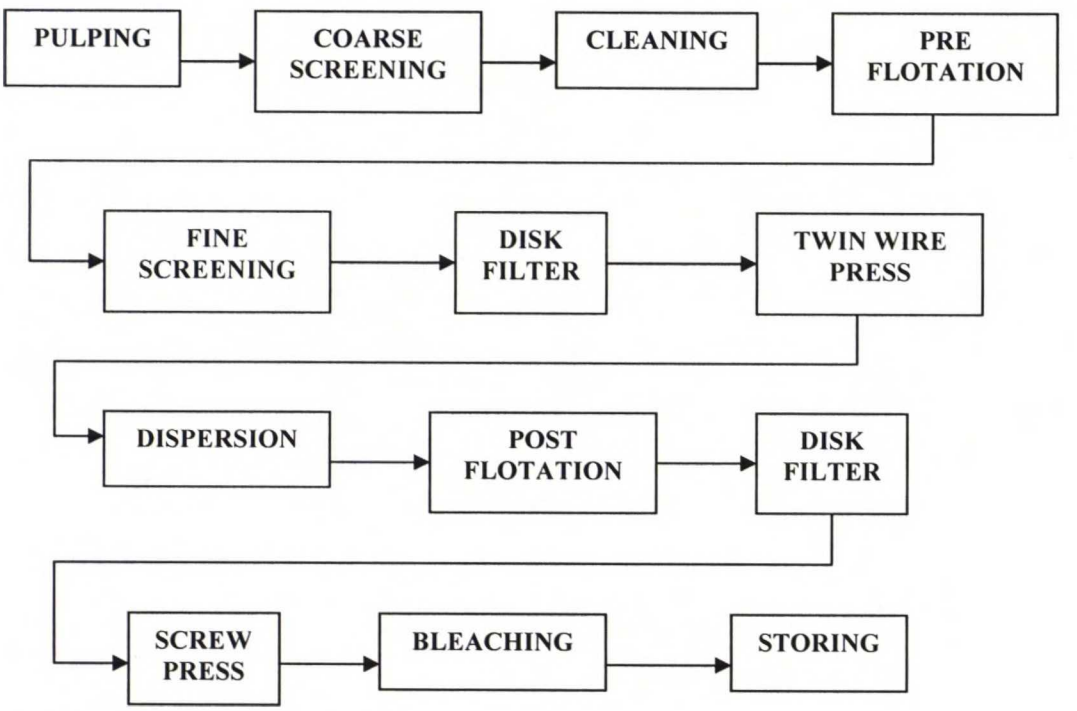

Figure 1. Example of a deinking process.

For washing deinking and flotation it is essential that the pulp suspension has low consistency so that it is easier to remove the contaminant particles. Dispersing is easier to do in high consistencies and then the results are also better because the fibres are more flexible and survive the mechanical treatment with fewer damages. In deinking certain chemicals are needed to remove printing inks. Chemicals are preferred to add in thick pulp because less water means higher consistency of chemicals thus they are more effective and smaller dosage amounts can be used so it is also more economical. With water also dissolved material, which can influence negatively the bleaching reaction, is removed from the process /6/. There are a lot of chemicals which can be used in deinking process. The commonly used chemicals are presented in chapter 3 (Deinking process chemistry) of this paper. The quality and characteristics of the produced pulp are influenced by the process conditions and the raw material used. Recovered paper can include many different types of paper grades, printing inks and printing mechanism used. To ensure the quality of recycled pulp and the smoothness of the deinking process the recovered papers must be sorted. Not always is this possible. The deinking process has to take into account what kind of raw material is available. Also legislation and cost-effectiveness are driving forces when deinking plant is designed or operated.

2.2 Subprocesses

2.2.5 Pulping

The purpose of pulping is to break down the recovered paper into individual fibres with the help of water, chemicals and in some cases heat, at least to such a degree that the suspension is pumpable. Also coarse contaminants are removed from the raw material at this stage. The operation is intended to be done with minimum fibre damage and contaminant degradation. The pulper works also as a chemical reactor. The chemicals needed at the beginning of the deinking process are added into the pulper. It is preferred to do pulping in higher consistencies because this gives higher consistency also for the chemicals, saves steam, generates less fines and contaminants tend to stay in largest possible form /7, p.35/. Pulping and

slushing can be done in batch by pulpers or continuously by drum pulpers. /8, 9/. In batch pulping the residence time for fibres is the same for each batch therefore it is used for creating uniform and complete defibering, or when chemical reaction must take place /9, p.18/. With drum pulpers higher production can be achieved for a given size of pulper but the defibering is less uniform because of the normally distributed residence time /9, p.18/. Wet breaking length is a critical parameter for pulping. Due to a different water absorption potential for various paper grades, mixed recovered paper requires different pulping time. /8/.

Pulpers are usually cylindrical stainless steel vats containing an impeller with blades for mixing and defibering, and auxiliary equipment for removing coarse contaminants. An example of a pulper is shown in figure 2. On the vat walls there are vertical and/or guide elements to create a better flow circulation to the pulper center. The pulping forces are created by the rotating impeller with, in some cases, the help of impact bars on the vat floor. The impeller's peripheral speed is 12 - 20 m/s /8, p.97/. Pulpers can operate at three different consistencies: at high consistencies (HC) up to about 19 % stock consistency, at medium consistencies (MC) up to about 12 % stock consistency or at low (LC) consistencies up to about 6 % stock consistency. LC pulpers mostly operate continuously. /8, 9/.

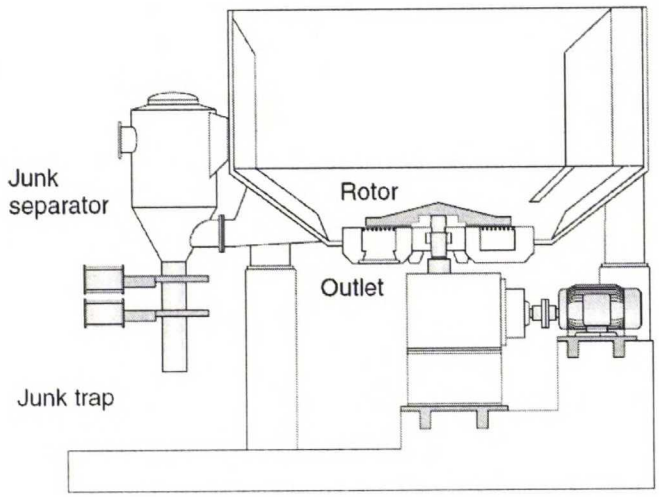

Figure 2. Low consistency pulper. /8, p. 97/.

Drum pulpers are used for recovered paper grades with low wet strength. They require space because of diameters of 2.5 - 4 m and lengths of up to 30 m. A schematic arrangement of a drum pulper is presented in figure 3. Drum pulpers rotate at circumferential speed of 100 - 120 m/min /8, p.105/. Drums are rotated with the help of friction using truck tires or with gear ring and pinion. The drum is divided into two zones, the first zone covers two thirds and is for pulping and the rest of the drum is the screening zone. The consistency in the pulping zone is about 14 - 20 %. The shear forces occur from the flowing or rolling motion as the drum rotates. The greatest pulping forces appear when the stock falls from the top of the drum. The process is gentler compared to pulpers; therefore the contaminant particles remain large enough for good screening. In the screening zone, the stock is diluted to consistency of 3 - 5 %. /8, 9/.

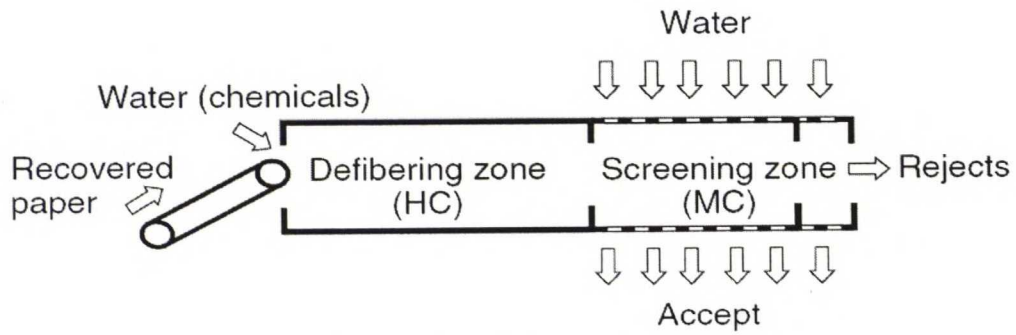

Figure 3. Schematic arrangement of a drumpulper. /8, p. 104/.

2.2.6 Screening and Cleaning

The purpose of the screening is to move trash and debris from the pulp slurry after pulping. Screening is usually separated into two screening steps, coarse and fine screening /7, p.36/. The screening stage is composed of several screens. The screen types are selected according to the debris concentration of the pulp slurry coming in, required pulp quality and fibre losses. The screening systems can be arranged as cascade or as feed forward. The cascade system is a counter current system where the accept from the secondary stage is returned to the primary feed, the tertiary stage is returned to the secondary feed and so on /10, p.37/. In the feed forward system, the accept of each stage is going to the production level and reject

is fed to the next screen. The feed forward system reduces the capital and operational costs and has higher efficiency than the cascade system /10, p. 38/. Both cascade and feed forward systems can be seen in figure 4.

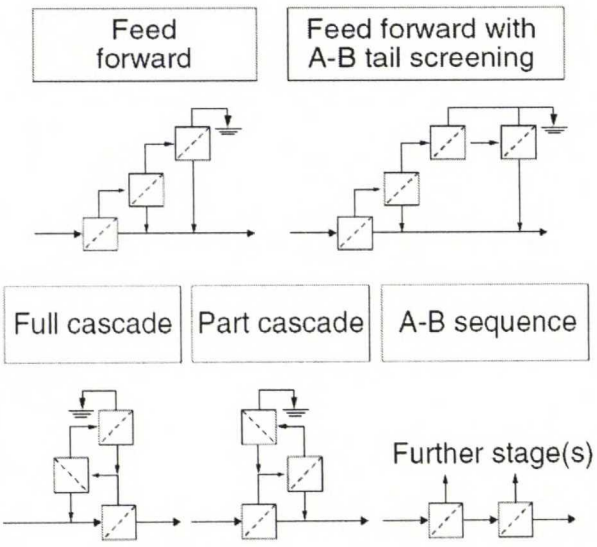

Figure 4. Screening system diagrams for recycled fibre pulp processing. /8, p.130/.

The coarse screening is most often started already in pulping where big objects like heavy particles, plastic foils and bailing wires are removed from the slurry. The rest of the steps are done with disk and cylindrical screens which operate under pressure. There are also other types of screens but nowadays pressure screens are most common. Disk screens are used for pulp slurries with high trash and flake content to minimize fibre losses because they have higher deflaking potential compared to cylindrical screens which on the other hand are used for rather clean pulp slurries and when high accept cleanliness is demanded. The coarse screens have holes in the range of 1 - 2 mm and they operate at the consistency of 3 - 5 % /10, p. 29/. At the final stages of coarse screening system all debris particles enriched from previous stages must be removed otherwise they move forward to production level /8, p. 122/. For this process stage final stage coarse screening machines are used. They are designed to handle high trash content with minimum fibre loss and have high deflaking potential /8, p. 123/.

The fine screening usually follows coarse screening and is done at low or medium consistency; screen baskets with slots in the range 0.1 - 0.15 mm are used. Even smaller slots are available to ensure the cleanliness of the pulp but for the time being the fibre loss is considered to be too great. The purpose of fine screening is to remove very small contaminants like pieces of plastic, stickies and specks. /8/.

Centrifugal cleaning is done with hydrocyclones whose purpose is to separate high density and low density particles. Other characteristics for particles to be removed with centrifugal cleaning are specific gravity, size, shape and deformability. The particle separation in hydrocyclones is based on centrifugal flow. The pulp slurry is fed tangentially into the hydrocyclones through an appropriately-shaped inlet which converts the pumping energy into a swirling motion. The ring vortex moves down to the conical section of the cyclone, inside of this the flow forms an inner spiral with reverse axial direction. The particles of higher density than water migrate to the ring vortex and are ejected from the bottom of the hydrocyclone. The rest of the pulp slurry moves with core vortex towards the vortex finder at the top of the hydrocyclone and is discharged from there. A hydrocyclone and the flows inside of it are shown in figure 5. /8, 11/.

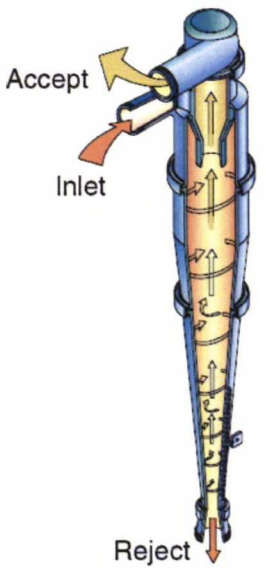

Figure 5. Cleaner for HW particle removal at low pulp consistencies. /8, p. 135/.

High consistency cleaners are used after pulper screen for pre-cleaning. They remove coarse heavy particles such as metal, sand and glass particles. The pulp consistency for HC cleaners is about 2 - 5 %. The medium consistency cleaners operate at consistencies up to about 2 % and are used for removing heavy particles like paper clips. Low consistency cleaners operate at consistencies of 0.5 - 1.5 % and can be used for removing very small heavy or light particles. There are also combination cleaners which remove both heavy and light particles. When particles with lower density than water are separated, either reverse or centripetal cleaning is used. Centripetal separation is based on the same principles as centrifugal separation, the only difference is that the heavier particles are now in the accept flow. In reverse cleaning the accept comes out from the bottom of the cyclone. The low density cleaners are situated after flotation or washing and they operate at low consistencies. Cleaners can be connected in parallel to form cleaner batteries when throughput is high. Cleaners are usually organized in cascade systems. /8, 11/.

2.2.7 Deinking

The purpose of flotation and washing deinking is to remove ink and toner particles from the pulp slurry so that the fibres can be used again in paper production. After pulping the recovered paper into fibres and removing trash from the pulp slurry, the ink particles can be removed. To separate the ink from fibres two techniques can be used: flotation or washing. Before flotation became more widespread washing was a predominant method and is still rather popular in the United States.

Flotation deinking is done in flotation cells with the help of chemicals and air, it is the most selective and efficient method for removing ink particles. There are various types of flotation cells available: they can be open or closed, different methods are used for removing the froth and supplying the air into the system. The performance of the flotation cell depends on optimization of pulp aeration, air removal and subprocesses of reject removal. The basic idea of flotation deinking is to alter the surfaces of the ink particles and other contaminants in the

suspension hydrophobic, unless they initially are. The alternation is done with suitable chemicals. Hydrophobic surfaces are needed so that the contaminants can attach to each other forming agglomerates and/or to air bubbles to rise with them to the surface of the suspension where the froth formed can easily be removed. Flotation does not separate hydrophilic particles, like fibres. The deinking chemicals are often added to the process already in pulping. Sometimes some soap is added to pulp slurry just before it goes into flotation cells mostly to control the froth. In suspension the particles have to be loose and move freely to enable good flotation results, therefore the consistency is low in flotation. Ink particles are already pretty much detached from the fibres because of the chemicals loosing the chemical bonds, the fibre swelling breaking the ink formation and the mechanical friction in pulping. The size of the contaminant particles has to be 10 - 250 μm so that the flotation is still efficient. Larger particles to some extent can be removed but smaller particles have to agglomerate onto each other or onto larger particles to be able to be removed. To advance the agglomeration some collector chemical like soap can be used /8, 12/. Figure 6 shows removal efficiency for different sizes of particles in various unit operations of the deinking process. The consistency of the suspension in flotation is about 0.8 - 1.5 %. Temperature is in the range of 40 - 70 °C, the pH should be about 7 - 9 and the water hardness 5 - 30 °dH when fatty acid surfactants are used. /8/.

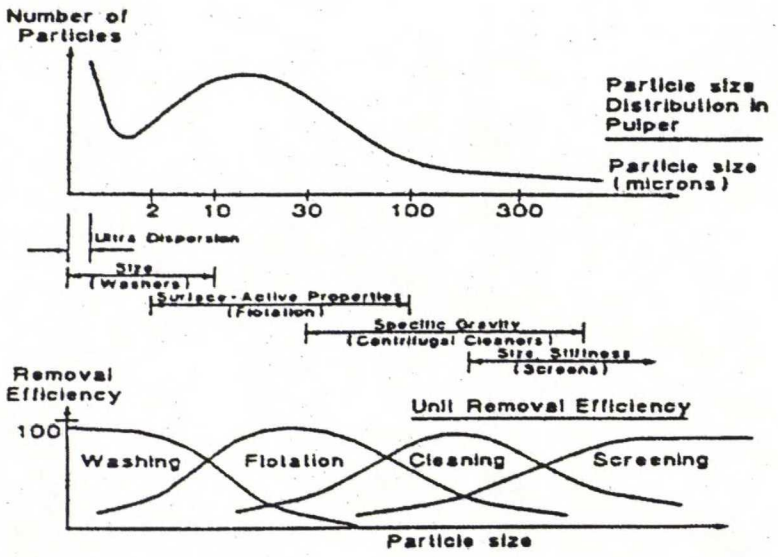

Figure 6. Ranges for optimal particle size for various unit operations in deinking. /13/.

Flotation probability can be divided into four stages each having its own probability. To remove the contaminants from the pulp slurry, the particles have to collide with an air bubble, attach firmly to it, rise to the froth layer as a stable aggregate and be removed with the froth /8, p153/. The number of air bubbles increases the probability of their collision with particles. Also the size of the air bubbles counts, to transport big particles big bubbles are needed. When particles are in relative motion with bubbles and approach close enough, attachment is possible. For firm attachment a three-phase limit must be fulfilled and equilibrium reached then stable transport is possible. Hydrodynamic flow forces try to remove particles from the bubble's surface and succeed if the particle is not adhered firmly. The aggregate also has to be stable enough to withstand the changes in surface tension and the forces of removal from the surface of the suspension. If the bubble bursts the adhered particles are liberated back to the suspension. In figure 7 is shown a model of ink particle impact and sliding collision with air bubble. /8, 12/.

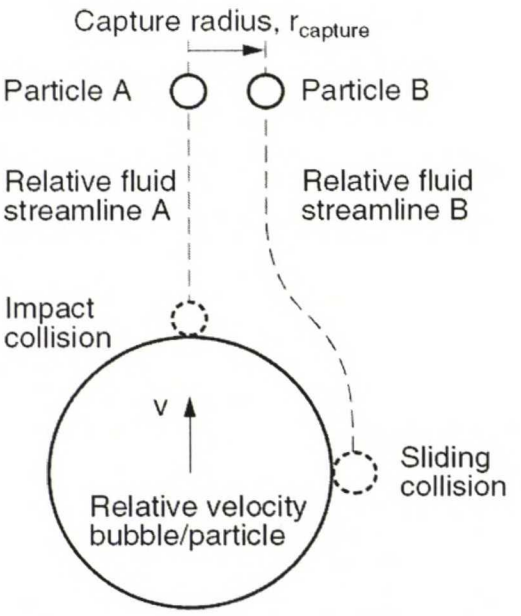

Figure 7. Stream lines and collision conditions between particles and bubbles. /A, p. 154/.

Washing can move printing inks, stickies and fillers to some extent but is not as efficient a method as flotation. In wash deinking the pulp slurry is filtered against a wire and particles smaller than 30 μm are flushed through. The aim of washing

is to remove undesirable substances such as ink and coating particles, micro stickies, dissolved and colloidal material and also fines and fillers. The quantity removed of the last two is often observed because it is not always desirable to remove all fines and fillers. Washing is mainly used for ash removal when deinked pulp is meant for tissue paper production; it is also the preferred deinking method in North America. As in flotation, in washing the particles to be separated have to be detached from fibres. The basic mechanisms of flotation and washing are shown in figure 8. Washing has its advantages when it comes to removing ink from flexographic printed papers. The flexo ink particles are small and water-based i.e. hydrophilic and for that reason difficult to remove with flotation but ideal to be washed out. /8, 14/.

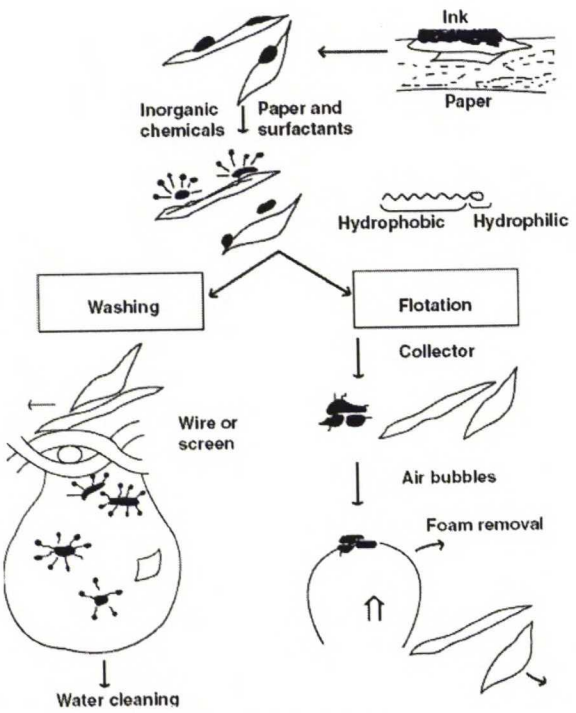

Figure 8. Deinking by flotation or washing. /15, p. 241/.

A number of different kinds of devices can be used for washing; screening and filtration are the main principles. Highly turbulent washers are more efficient in the removal of small particles because they hinder the formation of the fibre mat. Washing is often related to thickening and dewatering. The difference between washing and dewatering is that they remove different kinds of solids from the suspension. The purpose of dewatering is to separate process water from the fibres

and increase the consistency of the pulp slurry where as in washing solids fractions are separated from one another and unwanted contaminants removed from pulp slurry. The machinery does not vary much for these operations. /8, 14/.

2.2.8 Thickening

As water is removed from the pulp in dewatering the consistency increases and so the pulp gets thicker. That is why dewatering can also be called thickening. Thickening or dewatering precedes dispersion and bleaching to make these procedures more efficient and economical /14/. The purpose of dewatering is also to separate process loops from each other. To increase the pulp consistency the pulp slurry is filtrated or pressed, usually both. Disk filters, like one presented in figure 9, are commonly used to separate process water from pulp slurry and also separate water loops.

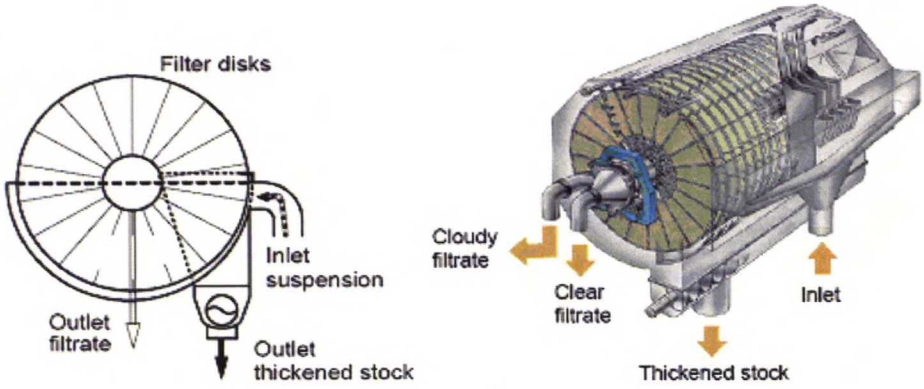

Figure 9. Principle and schematic arrangement of a disk filter /8, p. 174/.

In filtration, a filter mat from fibres is formed on the top of a wire or a screen while water and some fine solids go through to the filtrate. As the filter mat thickens filtrate time increases and less solids and liquid go through, so the throughput decreases while flow resistance increases which means that the dewatering becomes more complicated. Heating reduces viscosity of water and hence improves water removal. Filtration can be based on gravity, pressure differential, mechanical pressing or centrifugal force. When pressure is added to

help the filtration, the machinery often used is e.g. screw presses or twin wire presses. Cross section of a screw press is shown in figure 10. /8/.

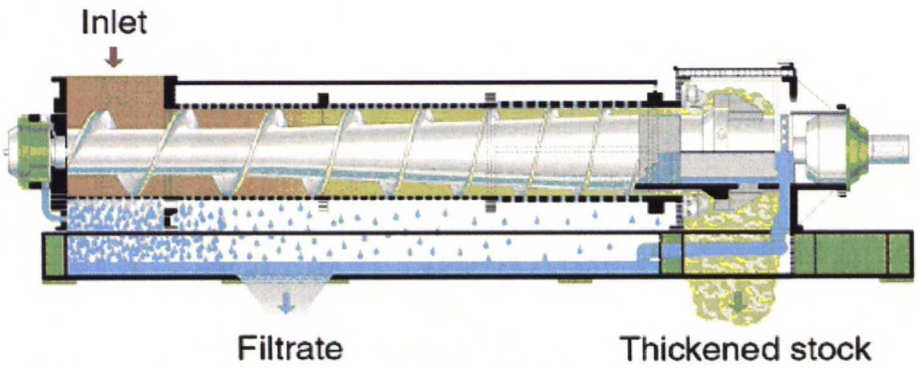

Figure 10. Cross section of a screw press for stock dewatering /8, p. 175/.

2.2.9 Dispersing

The purpose of dispersing is to break down the contaminant particles so that they can be either dispersed into the pulp or detached from fibres to be removed in other process stages. When the contaminants are hidden in the pulp, the brightness of the pulp decreases. Dispersion also makes the stock more homogenous /16/. The dispersion stage follows thickening because for dispersing the stock consistency must be 22 - 30 % so that the necessary amount of dispersing energy can be transferred onto the stock. Otherwise the shear forces will not be high enough to have the required effect on fibres and debris. Dispersion can be done before deinking as well to release ink and coating from fibres and make particles smaller so that they are easier to remove in flotation /17, p.141/. This treatment is not recommended for newspapers because the ink used will stain the fibres grey. Usually the dispersion stage is located between deinking stages or after deinking /16/. In hot dispersion thermofusible contaminants are dispersed and the hot dispersion stage is often combined with bleaching. High temperatures ensure microbiological decontamination and also improve the dispersing result because the particles get softer and are easier to disperse. The dispersion temperature varies according to requirements of the dispersion. Without any heating the temperature is about 40 - 60 °C, in most cases the temperature is raised with steam to 90 °C. /8, 17/.

There are two types of dispergers, disk and kneading dispergers shown in figure 11. Although dispersing is based on strong enough shear forces the two disperger types are very different. The disk disperger reminds disk refiners used in mechanical pulp production, the fillings are only bigger. The kneading disperger or kneader is horizontal and the rotor fillings are much greater than those for disk disperger. The operating speed is significantly slower compared to disk disperger also the mechanisms differ. Kneaders seem to leave stickies untouched where as disk dispergers breaks them down to a dimension where they are no longer visible or can be removed in other stages of the whole deinking process. Disk dispergers improves strength characteristics, sometimes also refiners are used because of that. Dispergers and kneaders are also used mixers for bleaching chemicals. /8, 17/.

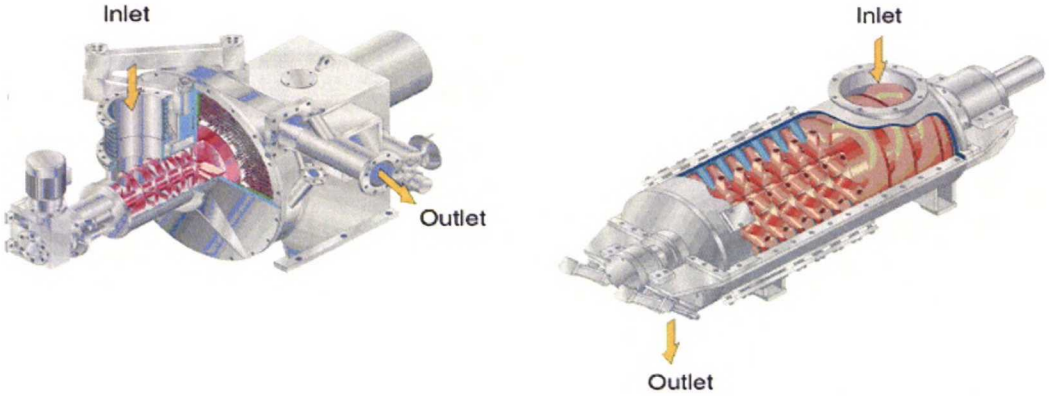

Figure 11. Disk disperger on the right and single-shaft kneading disperger or kneader on the left. /8, p. 189 - 190/.

2.2.10 Bleaching

The bleaching stage is usually situated quite at the end of the whole deinking process; it can even be the last stage before storing and/or moving forward to the paper production process. Bleaching is done at high stock consistency because it enables the use of less chemicals and a shorter retention time is needed. For economic reasons bleaching is used only when the end product requires improved optical characteristics. Mixing and point of addition are very important for the success of bleaching. There is usually a separate stage for bleaching but for

example peroxide can be added into the disperger. Due the efficient mixing in the disperger the bleaching chemicals are effective. Bleaching can be based on both oxidative and reductive bleaching processes. There are several factors influencing the bleaching process conditions and what kinds of chemicals are needed. These factors are, among others, the recovered pulp grade and its contaminants. /6, 18/.

There are many types of chemicals for bleaching: mostly used are hydrogen peroxide and sodium dithionite, chlorine-containing chemicals as well are used in United States. Oxygen and ozone bleaching can be used but because of their lignin-degrading effect only for wood-free recovered pulp. The chlorine-containing chemicals have the same effect and therefore are not used for bleaching wood-containing recovered pulp. For old news paper (ONP) and old magazines (OMG) peroxide and hydrosulfite are the bleaching chemicals used. Sometimes chelating agents are added to hinder the reaction of metal ions with peroxide. The chemicals and their function are covered more detailed in chapter 3 (Deinking Process Chemistry). /6, 18/.

2.2.11 Water Cleaning

For cleaning the process water and effluents microflotation, also know as dissolved air flotation (DAF), is used. The purpose of water cleaning is to separate solids from the liquid as well as possible. Flotation in water cleaning is based on the same principles as in deinking; the particles attach themselves on air bubbles which will rise to the surface and then the particles can be removed from suspension. Air is diluted into the water under pressure so that there will not be any air to reduce the flotation efficiency by collecting the small air bubbles needed to remove colloidal impurity. The amount of air dissolved in water depends on pressure and temperature. When the aerated water is depressurized back to atmosphere pressure it causes small air bubbles to appear. As the aerated water is then mixed with the unclarified water, the contaminant particles will attach onto the appearing air bubbles and rise with them to the surface. The sludge layer on the surface is stable and can be removed with a paddle. The clarified water is removed near the bottom below the rim of the clarification tank. With the

help of flocculants, anionic trash and fines are agglomerated into flocs and are easier to remove. When dual dosing is used colloidal substances are also removed from the water. /19/.

2.3 SE Sachsen

A block diagram of the deinking process of the Stora Enso Sachsen GmbH mill is presented in figure 12. In this figure also the addition points of chemicals are shown as well as what chemicals are being used. It is a two loop system with two production lines.

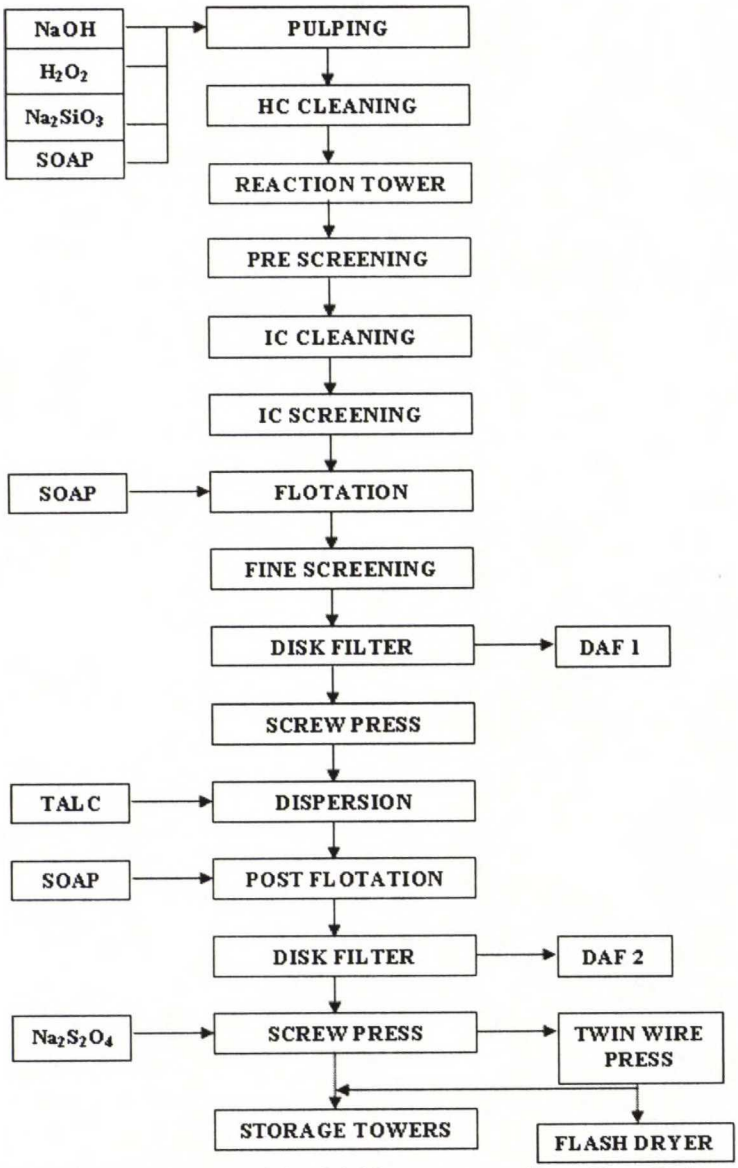

Figure 12. Simplified block diagram of the deinking process at Stora Enso Sachsen GmbH.

The available furnish consists of old news paper (ONP) and old magazines (OMG) of both at least 40%, normally the relation is 50/50. The recovered paper is pulped in two drum pulpers for ca. 20 minutes; chemicals are added to help the defibering and detaching ink from fibres. On top of defibering also first screening stage is in drum pulper. After drum pulpers the defibred material goes through high consistency cleaning which removes heavy particles, like glass, sand and staples. From there the accept pulp goes to reaction towers so that the chemicals added in pulping have time to act. There are two reaction towers with the capacity of 750m^3, the residual time is dependent on the production speed but is normally about 45 minutes. Before flotation the pulp goes through several cleaning and screening stages. From reaction towers the pulp is first processed through pre screening featured with holes, the diameter of the holes is 1.2 mm. Pre screening has three stages with a chest between each stage and it works with forward flow. IC-cleaners following remove particles heavier than the fibres. IC stands for intermediate consistency. The cleaners have four stages and work with cascade. From there the pulp goes into IC- screening with slot screens with the slot width of 0.2 mm. The IC-screening has three stages and forward flow with partial cascade, the accept from the last stage goes back to the inflow of the first stage. The pulp from the IC-screens is then passed through the storage tanks to the flotation cells for ink removal. The pulp from the storage tanks is diluted from ca. 1.8 % to ca. 1 % consistency for the flotation. The flotation time is slightly over 1 minute. The secondary pre flotation is used to collect back to the process the fibres lost in flotation as much as possible. The pulp brightness before flotation is between 48.8 - 49.5 %ISO and after flotation is 56.5 - 57.2 %ISO.

The flotation accept is passed to the fine screening with slotted pressure screens, which remove small particles e.g. stickies and remained ink particles. Fine screening consists of four stages with a chest in between each stage and is arranged as feed forward. The screens have two baskets inside; the slot width of the inner screen basket is 0.2 mm and for the outer screen basket 0.15 mm. After fine screening the pulp is thickened from 1 % to 30 % consistency through disk filters (1 % to 9 %) and screw presses (9 % to 30 %). The filtrate from these

stages is sent to the clarifier so that the water can be reused in the preceding process. The thickened pulp is dispersed before post flotation to break up stickies and other contaminants to be removed in post flotation. After disperging the pulp is in ca. 5 % consistency and is diluted to ca. 3.5 % consistency for the storage tanks before post flotation. For the post flotation the pulp is diluted to ca. 1.2 - 1.3 % consistency. Also post flotation has secondary flotation to collect fibres from the post flotation's reject. After post flotation the brightness is 60 - 61 %ISO. The pulp slurry is once again thickened from ca. 1.3 % to 30 % consistency with disk filters and screw presses. If the pulp is to be dried, it is thickened to ca. 45 % consistency with twin wire press and the filtrate is transferred to clarifier for water reuse in the process. Because the water removal decreases brightening some dithionite can be added to the screw presses to regain brightness. The final brightness lies between 58.5 - 59.9 %ISO. The thickened pulp goes to storage towers before being used in the paper machine. Part of the pulp goes occasionally from disk filters to twin wire press and from there on to flash dryer. The flash-dried pulp is pressed and packed for selling.

The microflotation for water cleaning does not use a dual system but only cationic compounds are added to make the flocculation of the contaminants possible. Bentonine is added first and then cationic polymer. Because the total amount of negative charges in the filtered water, which is to be treated in microflotation, is high a lot of cationic compouds are needed to neutralize the charge and because polymer is rather expensive it has partly been compensated by cheaper bentonite.

There are three flotation lines in pre flotation and two lines in post flotation. Two types of flotation cells are used in the deinking process of SE Sachsen, Voith Sulzer EcoCell and Sulzer Escher Wyss CF-Cell. These cells are different in structure and thus also in mechanical function. The first two lines of pre flotation and the both lines of post flotation have CF-Cells. The third line of pre flotation and both secondary flotations have EcoCells.

Sulzer Escher Wyss CF-Cell has two cells one on top of the other. In figure 13 the mechanical function of CF-Cell can be seen. The inlet is on the top (Stoffzufuhr) and the air is absorbed into the process as the stock flows through the diffusers (Nr. 1). The aerated stock is fed as tangential flow into the cell (Nr. 2) where the accept is collected from the bottom (Nr. 3) while the air bubbles form froth that collects the ink particles to the surface of the suspension. The reject flows out through the pipe in the middle shared by the two cells (Nr. 4). The showers (Nr. 6) break the froth and prevent formation of sediment. /20/.

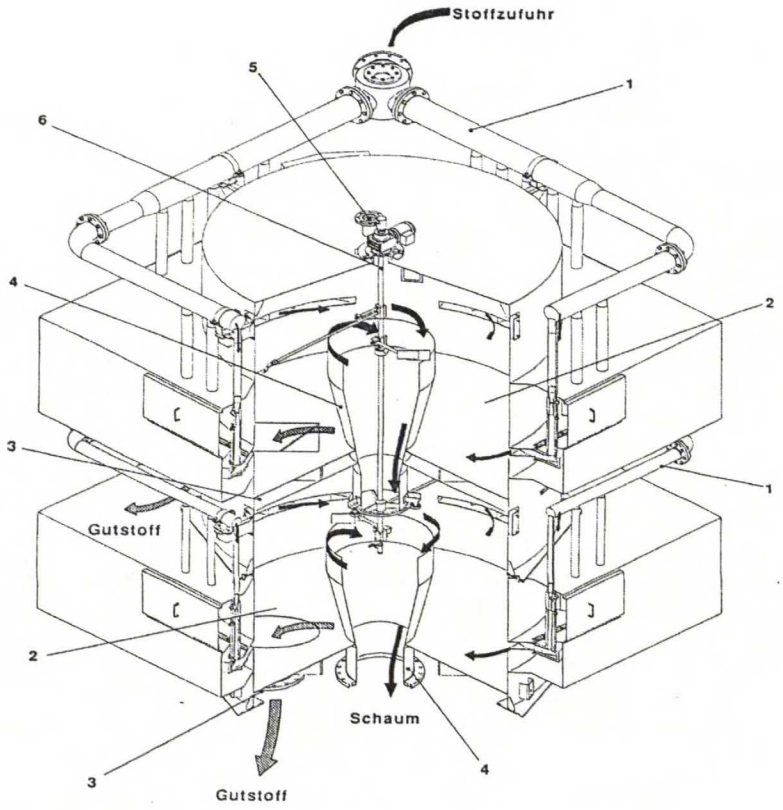

Figure 13. Mechanical function of Sulzer Escher Wyss CF-Cell. /20/.

Voith Sulzer EcoCell combines the advantages of its two predecessors, E-cell and Compact Flotation cell /21/. It has the high efficiency of the CF-cell and the simple control strategy with maximum operating reliability of the E-cell. EcoCell has same aeration principle as CF-cell applied to the inside aeration element of E-cell. The EcoCell is shown in figure 14.

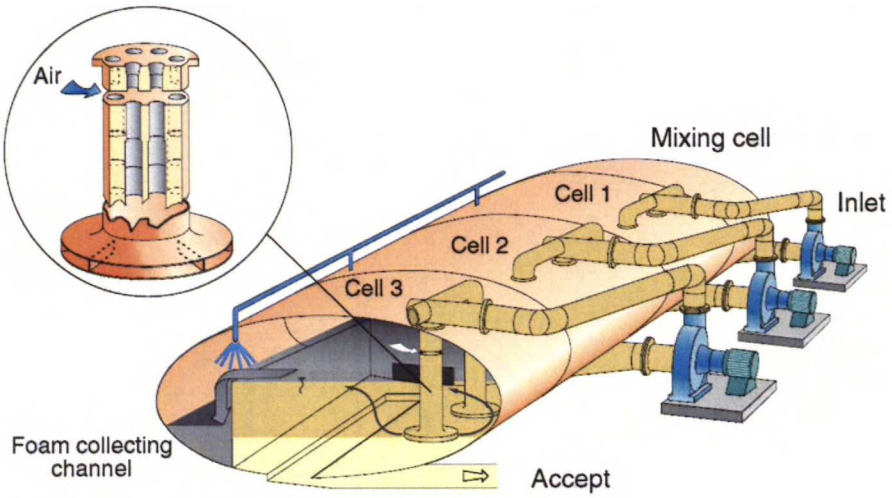

Figure 14. Basic function of the Voith Sulzer EcoCell. /8, p. 165/.

The EcoCell consists of individual cells in a row. The inflow to the first cell flows through aeration system similar to the CF-Cell. The reject flows over into the collecting channel as the accept is pumped from the bottom to the next cell through an aeration system and so on until the last cell. From there the pulp suspension is pumped into the next process phase. The flotation cells are connected with each other by a hole in the walls between them. The holes are under the suspension surface and through the holes suspension can flow back to equalize the cell level. The showers over the froth collecting channel break the froth decreasing the volume of the reject flow to the sludge collector. /22/.

3 DEINKING PROCESS CHEMISTRY

3.1 General Overview

In the deinking process several different chemicals can be used in different parts of the process. Chemicals are added to the process according to the need for them. Nothing is added unless it is necessary because chemicals can also have a negative effect. The doses of chemicals are usually given as a percentage on bone dry pulp. In table 1 are listed the most usual chemicals used in deinking process and their purpose. Of course the use of chemicals is dependent on the recovered paper available and other process factors; legislation and economics have their role too.

Table 1. Common deinking chemicals and their function.

Chemical	Function
NaOH	pH rising, fibre swelling, saponification, ink break up
H_2O_2	prevention of yellowing, bleaching agent
fatty acid	raw material of soap, ink dispersion and collecting
Na_2SiO_3	buffering, preventing ink redepositioning, stabilizing conditions where peroxide works
Surfactants	fibre wetting, stabilization of detached ink particles

Chemicals added to the pulper assist the pulping process by breaking the fibre net and removing undesirable material. The higher the consistency during pulping, the lower the dosages of chemicals needed. Less water in pulping means higher concentration of chemicals in which case smaller dosage amounts can be used. Pulping is an important process stage, it is even said to be the "brains" of the process /23/. Nearly 70 % of the chemicals used in the process are added into the pulper or drum pulper and some 22 % of the chemicals are used in the dispersing and post bleaching /24/. Not only chemicals and their dosages are important for successful pulping but pH, temperature, time and stock consistency play major roles, too /25/.

3.2 Pulping Chemistry

Sodium hydroxide, NaOH, also known as caustic soda, has the effect of swelling fibres and so it helps the break the bonds between fibres, it also detaches ink particles and coatings from fibres /25/. By swelling is meant that the fibres absorb water and become more flexible. Although the amount of caustic soda added to the pulping is given as a percentage on bone dry pulp it is not added according to the amount of fibres but to adjust the pH of the process to alkaline level. Sodium hydroxide also saponifies and/or hydrolyses ink particles; this could improve water solubility of the ink and cause swelling of binders used in printing inks /26/. Considering the performance of hydrogen peroxide, caustic soda has a great influence. On mechanical fibres the alkalinity has an unwanted effect, wood-containing furnish darken and yellow. The phenomenon is known as alkali darkening. Because of all the effects sodium hydroxide has, it is vital to pay attention to the dosing to get the best result possible with minimum detrimental effect. /25/.

Hydrogen peroxide, H_2O_2 is added to prevent the mechanical fibres from yellowing in alkaline conditions during pulping. It also helps in ink removing by breaking down cross-links between the alkyd binder molecules of the printing ink /24/. The conditions during pulping reduce peroxide's bleaching effect which is based on the perhydroxyl anion (HOO-). The perhydroxyl anion is produced when peroxide reacts with caustic soda according to the equation 1 /23, p. 77/:

$$H_2O_2 + NaOH \leftrightarrow HOO^- + Na^+ + H_2O \qquad (1)$$

To create the best conditions for maximizing the amount of perhydroxyl anion increased amount of peroxide, high pH and temperature are required. Because of the increased amount of peroxide, also the dosage of caustic soda has to be increased which cause more darkening of the wood-containing fibres. It is important to find the right ratio of peroxide to caustic soda to avoid alkali darkening and obtain maximum brightness /6/. Reducing the decomposing side reactions also improves the conditions for peroxide. Those side reactions are

caused by heavy metal ions. Stabilizing agents like chelants or sodium silicate (Na_2SiO_3) can be added to prevent the effect of heavy metal ions. Chelants are not so popular anymore because they pollute waters and it has been found out that most of the cases the metal content during pulping does not require chelants. /23/.

Sodium silicate, Na_2SiO_3 is widely known as water glass. It is actually a mixture of many complex polymeric silicon ions. It works as a buffering agent in alkaline conditions, during pulping it also disperses ink particles and prevents them reattaching to fibres thus increasing brightness. Water glass improves collecting and flocculating ink particles which also increases brightness /6/. Although it is said to stabilize peroxide, it actually stabilizes the chemical conditions where peroxide works. Even though the reaction mechanisms of water glass are not exactly known, it has been noticed that the use of water glass reduces flotation of fines and fillers thus affecting yield positively /6/. When dosing water glass, pH has to be considered as well as the amount of sodium hydroxide because both sodium hydroxide and water glass increase pH. According to previous there is a possibility to decrease the amount of sodium hydroxide by adding more sodium silicate. On the other hand, when too much is added, silicate causes problems at the paper machine like scaling and fouling of equipments because it likely reacts with alkaline products forming precipitants. Silicates are also dependable on temperature, it crystallizes when temperature drops so it is difficult to handle in cold waters, and in high temperatures it causes fouling. /23/.

Soap is made of fatty acid and for example sodium hydroxide, sodium soap is water soluble /15/. Soaps belong to the group of anionic surfactants /24/. Fatty acid soaps are used as collectors in flotation deinking, especially in Europe. The dosing points for soap are either pulper and/or just before flotation cells. When soap is added to the pulper, it gives collecting properties whereas dosed to the flotation soap acts more as a froth controller /15/. The purpose of soap and other collectors is to gather the ink particles removed during pulping so that the contaminants can be removed by air bubbles in flotation /30/. The collector chemicals also affect the surface tension of the air bubble which has to be steady

enough not to break until it reaches the surface. Before fatty acid can act as a collector it has to be converted from sodium soap into water-insoluble calcium soap. To achieve this, calcium ions are added as calcium chloride or calcium hydroxide into the process with soap. The slow reaction rate between soap and calcium ion supports addition to the pulper because when added to the flotation the reaction might be incomplete and then some soap would not act as collector. This addition is not always necessary because of the water hardness and the ash content of the recycled paper used, like is the case in SE Sachsen. What comes to adding calcium into the process, one has to be careful not to add excess amount because calcium ions are believed to cause e.g. scaling and yield loss. Excess calcium can react with other chemicals in the process forming different kind of calcium salts which cause deposits and scaling of the process equipments. Yield loss is said to be dependent on the water hardness in flotation son that higher water hardness causes higher loss /15/. It is not known for sure what the mechanism of calcium soap is; one theory is presented in figure 15. The sodium soap reacts with calcium ions and turns into insoluble calcium soap. The calcium soap precipitates on the ink surfaces giving them a more hydrophobic nature so that the ink particles agglomerate into bigger particles and attach on the air bubbles.

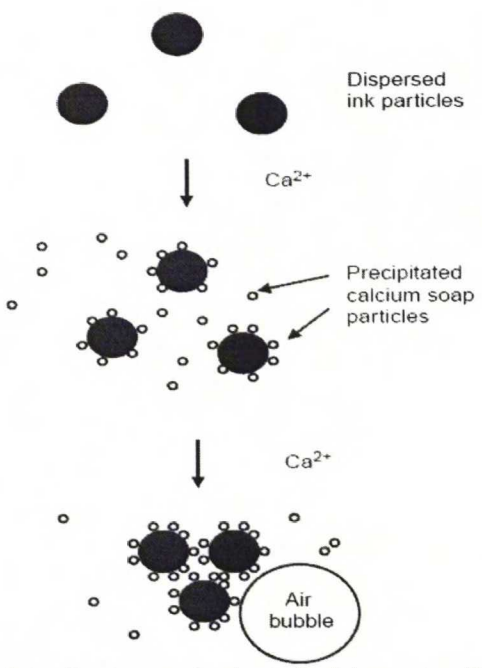

Figure 15. Hypothesis for the collecting mechanism of calcium soap. /15, p. 252/.

Delivering and storing of fatty acid can be problematic because fatty acid has to be over 70 °C so that it does not solidify /28/. Also in preparation of sodium soap the water and sodium hydroxide has to be heated before mixing with fatty acid. This all requires equipment and energy so the costs for using fatty acid soap have to be considered. The fatty acid can also be delivered to the mill as presaponified solid soap pellets or liquid soap /30, p.51/. In that case the preparation of sodium soap is easier or not needed, the pellets just have to be liquefied and the liquid soap is already in usable form. With using pellets there is a possible safety hazard from spilling. The liquid soap can cause high transportation costs. So what is reasonable has to be considered.

Emulsions are mixtures of fatty acid collectors and synthetic collectors, generally containing fatty acids, fatty acid derivatives, surfactants and water. These semi-synthetic collectors do not require certain calcium ion concentration but perform fine in soft water. Actually the fibre losses might increase when emulsions are used in hard water. Emulsions require a certain residence time to perform well in flotation; therefore they are most often added into the pulping. When emulsion is stored mixing is recommended but it is important not to mix air into the chemical because it foams easily. /15/.

Surfactants are surface active agents which mean they congregate at surfaces /4/. As the surfactant concentration in solution increases, the surface tension decreases. They are added into the pulper to decrease adhesion of printing inks to the fibres /15/. Surfactants are made up of two components, hydrophobic and hydrophilic component /23, 31/. The hydrophobic end dislikes water and attaches to the ink, oil and dirt particles where as the hydrophilic end likes water and remains there. This way they form micelles. The purpose of micelles is to keep the dirt and ink particles from reattaching to hydrophilic fibres. Surfactants have also several other functions in deinking. Addition to preventing the redeposition of ink particles, surfactants also work as a dispersant separating the ink from fibres, they act as a collector to agglomerate small contaminant particles, in flotation they form a froth layer at the top of flotation /31/. Surfactants can be anionic, cationic

or nonionic /15, 31/. This electric charge affects how the surfactant works. Many types of chemicals are included as surfactants; surfactant is actually a common term for uses like dispersants, collectors, wetting agents, displectors, and antiredepositions aids /23/. The use of surfactants is depended on their requirements, in deinking they can be added either into the pulper of just before flotation. When choosing the surfactants for a given process, the process temperature must be taken cognizance of. If the temperature is too high for the given surfactant, it starts to associate with surfactant molecules and the formed aggregates can be seen as milkiness or cloudiness in water. The phenomenon is known as cloud point. For characterizing surfactants the hydrophilic-lipophilic balance (HLB) can be used /25, 31/. It expresses the ratio in weight percentage between the hydrophobic and hydrophilic groups in the structure of surfactant molecule. When the HLB high is, the hydrophilic head is greater and being so, water solubility is high as well as polarity /4, 15/. And with low HLB values it is naturally vice versa.

There are dissenting opinions as to whether the use of surfactants in deinking is good or bad because they cause problems at the paper machine and accumulate on process waters but on the other hand, when it comes to deinking properties, they are efficient and in addition to that they are easy to handle.

Enzymes have been studied for the past two decades with the view to using them in deinking process. Enzymes are already in use in other industrial sectors e.g. the food industry. Promising results have been gained in laboratory scale trials using enzymes for deinking and although the function of enzymes is still partly unclear possibilities for industrial use exist. Mainly cellulases and hemicellulases have been studied although there are also other enzyme options like lipases und esterases /32/. The function of cellulases and hemicellulase is based on a peeling effect; they split the long polymer chains of cellulose and hemicellulose found in fibre into individual sugar molecules /33/. As the surface of the fibre comes off the ink is removed. In figure 16 is shown how the cellulase attacks the surface of the cellulose.

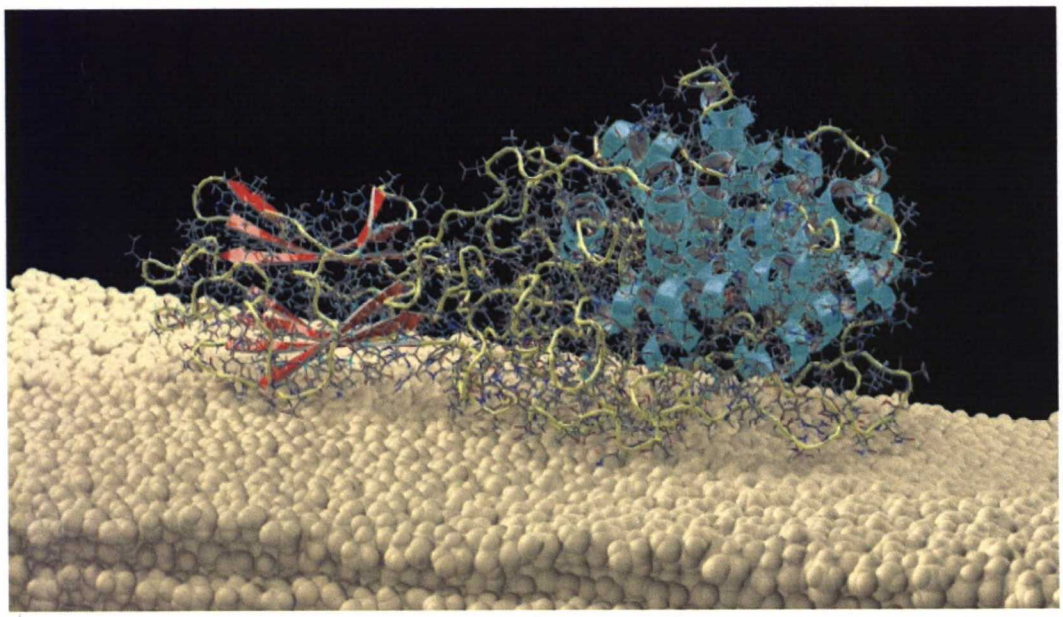

Figure 16. Cellulase enzyme in action on the surface of cellulose. /34/.

Although some fines and microfibrilles are removed with the ink particles it does not influence significantly the yield or strength of the produced paper /32/. Enzymes need to have contact with the fibre to be able to function therefore the fibres should undergo some mechanical treatment to open the fibre bondings before enzymes are added /35/. Enzymatic treatment decreases the demand for chemicals and energy in deinking as well as chemical oxygen demand (COD) of waste water.

3.3 Flotation Chemistry

Many of the actual flotation chemicals are dosed already into the pulper because of their requirement of residence time in order to work properly in flotation. As neutral deinking becomes more common, synthetic collectors e.g. surfactants, are becoming more important /24/. The combination of dispergator and collector called displector belongs also to the synthetic collectors which are very efficient dispergers in neutral deinking /26/. The synthetic collectors act as dispersants during pulping and as collectors in flotation /15/.

There is always a search for new and more efficient deinking chemicals. For example, Deng, Y. & Sun, G /36/ have studied the possibility of using

polydiallyldimethylammonium chloride (polyDADMAC) as the only deinking agent for ONP. At least the laboratory results were promising. PolyDADMAC neutralizes anionic substances to form small particles. No surfactant or calcium was needed and the removal of ink, ash and anionic trash is higher than with commercial fatty acid systems. PolyDADMAC can be used as flotation chemical in acid, neutral or alkaline process conditions.

Silicone derivatives are also a rather new invention in the area of flotation chemicals. They have been successfully introduced in several deinking mills in Europe. Silicon (Si), the basic element of silicone derivatives, is one of the most abundant elements on earth. The silicone derivatives are polysiloxanes, polymers composed of a Si-O-Si compound /37/. The basic structure of silicone derivative is presented in figure 17.

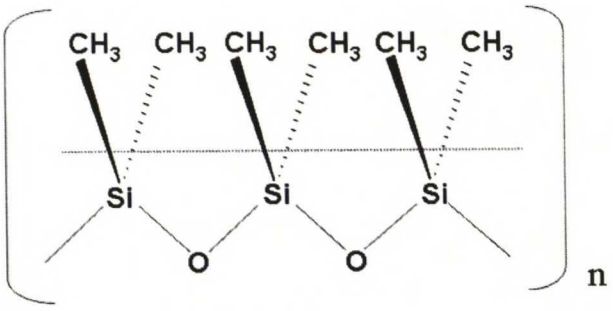

Figure 17. Basis structure of silicone derivative. /38/.

By modification with functional groups the silicone derivatives can be adjusted to particular purposes. The modification is necessary because the basis silicone polymer does not disperse in water and thus cannot be used in deinking /39/. The number of the methyl-groups substituted by EO/PO (ethylene oxide/propylene oxide) polymers in the silicone chain affects how the derivative performs. To ensure efficient performance it is important to dilute the silicon derivative before dosing to achieve homogeneous distribution. The process temperature needs to be at least 42 °C / 47 °C, depending on the product, because at lower temperatures the silicone derivative does not get its hydrophobic character needed to perform as collector. Silicone derivatives perform well also in neutral conditions and are independent of water hardness /28/. No special requirements are needed for

handling and storing of silicone derivatives because that can be done at room temperature. Even more cost savings can be achieved because with silicone derivatives it is possible to reduce the cost of collector because the dosage amount is considerably lower than with soap; silicone derivative 0.02 % whereas soap 0.3 % /29/. In laboratory trials made by the supplier of the chemical /29/ the silicone derivatives show selective flotation behaviour which soaps do not seem to have, this can promise a higher yield. According to those laboratory trials, silicone derivates are more selective towards ash which could mean that wanted ash content of the accept is achieved with a lower total loss and without negative influence on brightness. Decreased COD contamination because of lower process pH was observed in laboratory trials mentioned above as well as in implementing silicone derivative to mill scale production /28/.

3.4 Bleaching Chemistry

The purpose of bleaching is to increase the brightness of the deinked pulp by eliminating light absorbing materials /18/. To achieve this, there are several chemicals to choose from. The chemistry and number of stages needed depend on process conditions, recycled paper at hand and the required quality of the end product. Different bleaching agents work in different process conditions, so when adding a bleaching chemical to the process, it is critical to pay attention to the point of addition, mixing, consistency and pH to obtain the optimum result. The bleaching chemicals can be divided into two groups: oxidative and reductive. The first group includes chlorine (Cl_2), chlorine dioxide (ClO_2), sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2), oxygen (O_2) and ozone (O_3) /40/. The reducing agents typically are sodium hydrosulfite ($Na_2S_2O_2$) and formamidine sulfinic acid ($NH_2C(NH)SO_2H$). The oxidizing agents, excluding peroxide, are not suitable for bleaching pulp which contains more than 15-20 % mechanical pulp because of their degrading effect which causes yield loss /41/. There are also other bleaching chemicals, like peracetic acid (CH_3COOOH) and Caro's acid (H_2SO_5), and other methods, like enzymatic bleaching, which can be used for bleaching deinked pulp /6, 18/. The reductive chemicals and peroxide do not cause lignin removal and thus do not reduce yield. Instead they modify the chemical structure

of dyes making them appear colorless /40, 41/. In this paper the focus is on the non-degrading bleaching chemicals which are more commonly used in deinking mills in Europe.

Hydrogen peroxide, H_2O_2 has a low investment cost. It can be added to the pulper or be used as a post-bleaching agent at the bleaching tower. When added to the bleaching tower, peroxide is more effective than used in pulping /18/. A very good dosing point for peroxide in the deinking process is in the disperger. The conditions are ideal with high consistency, high temperature and good mixing; in addition the newly exposed fibre surfaces ensure an efficient bleaching effect. Peroxide decomposes rapidly when it comes in contact with contaminants so attention has to be paid to storing and handling. As peroxide decomposes it produces water and oxygen, because of this it is very favoured /40/. Peroxide does not remove lignin from the pulp; it just destroys the colour-causing groups. Otherwise peroxide has already been discussed in the chapter 3 (Deinking Process Chemistry).

Sodium hydrosulfite, $Na_2S_2O_2$ is commonly known as sodium dithionite or just dithionite. The optimal conditions for bleaching deinked mixed office waste (MOW) differ from those for deinked pulps containing mechanical fibres /18/. When bleaching mechanical fibres with dithionite, conditions of low consistency, temperature and pH (slightly acid) are often used. It is important to remove residual oxidative bleaching chemicals from previous bleaching stages before adding any dithionite, otherwise it will be decomposed. Dithionite can also react with oxygen or anaerobically with water forming corrosive thiosulfate ($NaHSO_3$). To avoid this, the dosing amount must be proper and the mixing effective and of course a separate bleaching stage is needed. By adding alkali decomposing reactions can be reduced /6/. Dithionite has the quality of being good colour-stripping agent for many paper dyes but it does not work well in high consistencies /40/.

Formamidine sulfinic acid, ($NH_2C(NH)SO_2H$), abbreviated as FAS, is the most effective of reductive bleaching chemicals. It can be added into pulper, disperger or bleaching tower /18/. For FAS conditions in a disperger with high temperature and mixing are also ideal. FAS is not sensitive to air but trapped air in the pulp might decrease the bleaching efficiency as well as residual oxidative bleaching chemicals which can react with FAS forming corrosive thiosulfate. FAS is delivered as powder so it has to be diluted /40/. The preparation of the solution is continuous and FAS liquor is added directly to the process because the liquid form is unstable. FAS is even a better colour-stripping agent than dithionite and the ideal circumstances for FAS are medium consistency and high temperature. The reaction product of FAS is urea, which is good for water treatment systems. The use of FAS is not that simple, it does not dissolve in water easily so the mixing has to dilute efficiently to get an effective bleaching agent. Alkaline conditions increase the solubility of FAS /6/. At high temperatures (80 - 100 °C) FAS performs more effectively and also lower dosages are needed. The cost of FAS is quite high but the dosage amounts needed are lower that with other bleaching chemicals /40/.

3.5 Additives

Talc is often used as a white filler in papermaking or as a pigment in coatings. Talc is soft, hydrous magnesium silicate /42, p.125/. Talc can be used for absorbing pitch in pulp or paper making processes. Because of its layered structure, magnesium sheet between two silica sheets, it has a hydrophobic face and the edges of the plate are hydrophilic /30, p. 56/. In deinking process it can be used for preventing the adhesiveness of stickies. Small stickies can adhere to the surface of talc and larges stickies are covered with talc.

3.6 Water Cleaning

Water cleaning has an important role in the successful operation of a deinking plant. Chemicals are used in water cleaning to get the best possible result. Mostly a two component system is in use /30, p. 55/. In dual systems two different

chemicals with different electrostatic charge are used; the cationic coagulant is often added first to collect dissolved and colloidal material, after that an anionic flocculation agent is added to form flocs from cationic floc fragments and other solids by bridging them /27, s.53/. The loose structure from bridging traps air causing the flocs to float.

Bentonite is a clay which has two types, sodium and calcium bentonite. It swells in water, the degree of swelling depends on salt concentration and cationic charge /42, p.123/. As the bentonite swells its specific surface area gets larger: because of this and the high ion exchange capacity, it is good in adsorbing dissolved and colloidal material in water clarification. Bentonite is used in water clarification instead of cationic coagulant for cost effective reasons /30, p. 55/. It is used together with anionic or nonionic flocculant, it also helps to reduce the BOD/COD in the effluent. Bentonite is also often used as a retention chemical in paper production.

Polymers used in paper industry can be cationic, anionic or nonionic and are water soluble /27/. There are many different types of polymers as well as additives for dry- or wet-strength in paper production that can be used either in retention systems or flocculants in waste water clarification. The polymers used as coagulants in water clarification are cationic in nature /30, p. 55/. In a dual system either anionic or nonionic polymers are also added, especially when bentonite is added first into the system.

4 TRIAL PLAN

The continually rising prices of fatty acids lead to the search for alternative chemicals for deinking. In this work the main purpose is to study whether silicone derivatives can be used in deinking process instead of chemicals based on fatty acid. Seven different types of flotation chemicals based on fatty acid are to be compared with a new type of flotation chemical based on silicone polymer of which there are two modifications. Three soaps and four different emulsions from different suppliers are tested. One of the soaps is produced and used here at the mill. It is made of a fatty acid which is plant-based. The second one is a soap made of fatty acid based on animal fat. The third one was actually still raw fatty acid and had to be saponified before using. All of the fatty acid based chemicals have been either considered or used in deinking process at this mill. Different dosing amounts and points for silicone derivatives are tested to find out the optimal dosage and whether the silicone derivative works better in pulping or in flotation.

Before the experimental part of this thesis could be started, a trial plan was laid out according to which the experiments would be done. This plan contains the chemicals and the amounts used for either pulping or flotation. The trial plan is represented in table 2. The variables in this test series are the chemicals, their dosing amounts and their dosing points. The dosing amounts are announced as percents of the dry content of the recycled paper. The dosing amounts for different soaps and surfactants are recommendations from the suppliers. The dosing amounts for sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2) and sodium silicate (Na_2SiO_3) are from the mill. The purpose of dosing different amounts of sodium hydroxide and peroxide is to try to affect pH and study the consequences.

Table 2. Trial plan.

pulping chemical, %	soap 1	soap 2, anim.	emulsion 1	emulsion 2	silicone derivate 1	silicone derivate 2	fatty acid (saponified)	emulsion 3(fresh)	emulsion 4	NaOH	peroxide	water glass	flotation chemical, %	soap 1	soap 2, anim.	silicone derivate 1	silicone derivate 2	fatty acid (saponified)
test point																		
0										0,25	0,5	0,8						
1	0,1									0,25	0,5	0,8		0,15				
2		0,1								0,25	0,5	0,8			0,15			
3			0,1							0,25	0,5	0,8		0,15				
4				0,02						0,25	0,5	0,8		0,15				
5					0,02					0,25	0,5	0,8						
6						0,02				0,25	0,5	0,8						
7										0,25	0,5	0,8				0,02		
8										0,25	0,5	0,8					0,02	
9										0,25	0,5	0,8				0,01		
10										0,25	0,5	0,8					0,01	
11						0,02				0,125	0,5	0,8						
12						0,02				0	0,5	0,8						
13						0,02				0	1,0	0,8						
14					0,02					0	0,5	0,8						
15	0,15									0	0,5	0,8					0,02	
16	0,075					0,01				0	0,5	0,8		0,075				
17							0,1			0,25	0,5	0,8						0,15
18								0,02		0,25	0,5	0,8						
19									0,02	0,25	0,5	0,8						

5 MATERIALS AND METHODS

5.1 Measurements

To be able to evaluate the effectiveness of the different chemicals several different measurements were made. All the measurements done in the laboratory trial are gathered in table 3. The table 3 also shows which measurements were done from which samples.

Table 3. Measurements made from samples to evaluate the efficiencies of different chemicals.

Measurements	Fresh water	Rejects	Flotated pulp slurries	Hyperwashed pulp slurries
pH	x		x	
water hardness, °dH	x			
volume, ml		x		
mass, g		x		
dry solids content, %		x	x	x
ash content, %		x	x	x
colour			x	x
ISO brightness, %			x	x
dirt specks, N/m² and mm²/m²			x	
ink elimination, %			x	

For some measurements filter pads and/or laboratory sheets needed to be prepared, those measurements are gathered in table 4. The methods used for measurements and preparations of filter pads and laboratory sheets are introduced in following paragraphs.

Table 4. Measurements made from filter pads and laboratory sheets.

Measurements	Filter pads	Laboratory sheets
dry solids content, %	x	
ash content, %	x	
colour	x	x
ISO brightness, %	x	x
dirt specks, N/m² and mm²/m²		x
ink elimination, %		x

5.2 Recycled paper

The recycled paper used in this work was collected household paper from Germany. The ratio used between old news paper (ONP) and old magazines (OMG) was 50/50. Before any trials could be done, the required amount of paper had to be torn hand into pieces of size ca. 2 x 2 cm. To get an equal paper mixture, enough paper should be torn for all the trials before starting. The pieces of paper were mixed and stored in a big plastic bag. Sorting was done by hand. The covers from magazines were removed as well as the staples, also all insert advertisements and samples were taken out before tearing the paper.

5.3 Fresh water

Fresh water was used for the experiments so that the laboratory trials would be comparable with each other. Fresh water contains the calcium coming into the production process. The water hardness of the fresh water has a crucial role for the success of the flotation when soap is used because soap needs calcium ions to be able to work as flotation a chemical. Fresh water was fetched from the paper machine with a big plastic barrel. The water had to be heated for the pulping and flotation. Before that the water hardness was measured with a photometric test using cuvettes and the method of Dr. Lange. Also the pH of the water was measured (ISO 6588:1981).

Part of the fresh water was heated to ca. 70 °C with a preserving boiler. The hot water was then mixed with the non-heated fresh water so that the temperature of the water used for pulping and flotation would be ca. 50°C, the same as in the real process. The temperature wasn't maintainable at that level, so after the flotation the temperature had dropped with approximately 10 °C.

5.4 Laboratory flotation

5.4.5 Preparation of chemicals

As the dosing amounts of chemicals are given as percents of the dry content of the recycled pulp, the amounts were converted to grams with the equation I

$$X = \frac{p \cdot n}{c} \qquad (I)$$

where X is the dosing amount of chemical (g)
p is the dosing amount of chemical as % of bone dry pulp (%)
n is the amount of recycled paper (g)
c is the concentration of the chemical (%).

To be able to weigh the smaller amounts (0.01 % – 0.02 %), the chemicals were diluted to 10 % consistency from 100 % consistency. The soaps were in solid form when weighed, and needed to be melted into a liquid form before using. That was done with the help of a hot plate. The consistency of the soaps used in this work was 7 %. The fatty acid used in test point 17 needed to be saponified first. The fatty acid reacts with sodium hydroxide as follows:

$$RCOOH + NaOH \rightarrow RCOONa + H_2O \qquad (2)$$

For the fatty acid used in soap 1 the molar mass is stated by the supplier to be 267 g/mol, it is assumed in this calculation that the molar mass of fatty acid is the same because the supplier is the same as for soap 1. For sodium hydroxide (NaOH) the molar mass is 40 g/mol, calculated from the periodic table. According to the chemical equation (2), 1 mol of fatty acid needs 1 mol of sodium hydroxide to form 1 mol of soap. The sum of the masses of chemicals needed for 1mol of soap is 307 g. Now the percentage value of both chemicals could be counted, for fatty acid that is 86.97 % and for sodium hydroxide 13.03 %. When, for example, 100 g of soap is produced, 86.97 g of fatty acid is needed and 13.03 g of sodium hydroxide. When soap of 7 % concentration is wanted, like in this trial, only 7 %

of each chemical is needed, that equals to ca. 6.09 g of fatty acid and 0.91 g of sodium hydroxide and the rest ca. 93 g is water. Because in this case the consistency of sodium hydroxide used in this trial is 50 %, two times more sodium hydroxide is needed to turn of the fatty acid into soap. Water on the other hand is needed a little bit less so that the target consistency for the soap remains. When soap is produced, there is always also water as reaction product so the soap is never exactly 100 %. This water amount could be taken into account when diluting the soap to the consistency needed. In this calculation that has not been done because the error it causes is small and the molar mass given to the fatty acid is an average anyway.

In producing soap and keeping it liquid the temperature has to be over 70 °C and constant mixing is needed. These conditions were met by using magnetic stirrer with a hot plate. The sodium hydroxide was first mixed with hot water and then the fatty acid was added to the mixture so that the chemicals do not react too furiously and splash out of the dose.

The soap Serfax RFA was made at the mill, also the sodium hydroxide, peroxide and sodium silicate used were from the mill. Other chemicals used in this work were samples delivered by suppliers.

5.4.6 Pulping

Pulping was performed with an industrial kneader. For a flotation 300 g of recycled paper was needed. Before turning the kneader on, 1760 ml of warm fresh water was poured into it, then the kneader was turned on and the paper was added as well as the chemicals according to the trial plan. After the chemicals were added a timer was set to 30 minutes. There was no reaction time between pulping and flotation. After the 30 minutes pulping time the pulp was added to the flotation cell which was already partially filled with some heated fresh water.

5.4.7 Flotation

A Voith injector cell as presented in figure 18 was used for flotations. From every flotation three samples were taken, 0-sample, 6min.-sample and 12min.-sample. There were also two samples of reject. To get the flotation started, first some warm fresh water was poured into the flotation cell and then the freshly pulped stock was added. After that the flotation cell was filled with warm fresh water up to 23 l. The mixing was started and the flotation chemical added according to the trial plan. The pulp mixture was let to mix for a while before taking the first sample, 0-sample. The sample was taken through a sampling valve, which was opened fully. The first few dl were poured back into the flotation cell and after that the proper sample was taken. In case of 0-sample, a sample of 2 l was taken. The 2 l of slush was compensated with 2 l of warm fresh water poured into the flotation cell. A measuring jug was put under the pipe where the flotation froth comes out and a timer was set to six minutes before the aeration was started. During the six minutes the wall of the flotation cell was continuously flushed with warm fresh water.

Figure 18. Voith injector cell for laboratory flotations.

After six minutes the aeration was turned off before taking the next sample, a 6min.-sample. Sampling was done as earlier but only one litre sample was taken and it was again compensated with warm fresh water. The measuring jug under the froth pipe was changed to an empty one before setting the timer again to six minutes and starting the aeration. Again the wall of the flotation cell was continuously flushed.

After another six minutes, altogether 12 minutes flotation, the aeration was turned off and the last sample was taken, 12min.-sample. The volume of the last sample was 2 l. After sampling and removing the measuring jug from the froth pipe, the flotation cell could be cleaned following the instructions of the manufacturer. At the end of the flotation there should be three samples of accept (0, 6min. and 12min.) and two samples of reject (0 - 6 minutes and 6 - 12 minutes). From reject only filtrated pads were made whereas from accept also laboratory sheets were made.

5.4.8 Hyperwashing

Hyperwashing is a common method to evaluate ink detachment. The ink content of a pulp sample is evaluated after intensive washing. A shower and a coarse wire are used for the process. After washing the pulp remaining on the wire contains very little ash and fines. /43/.

Hyperwashing was performed for 0- and 12min.-samples separately. One litre of sample, which dry content is about 10 g as the consistency of the sample is 1 %, was washed with the shower and a bucket containing a wire with screen opening size of 0.15 mm. Figure 19 presents the bucket and method used for hyperwashing in these trials. The temperature of the shower water was between 22 - 25 °C and the sample was washed for five minutes. After washing the pulp was gathered from the wire and diluted back to volume of one litre. Filter pads were made of the diluted hyperwashed pulp.

Figure 19. Bucket with wire of screen opening size of 0.15 mm and a shower used for hyperwashing.

Hyperwash was done to evaluate ink detachment. The evaluation was based on how efficiently the detached ink was removed in flotation. This could be done by comparing the brightness of 12min.-sample before and after hyperwashing. The potential of ink removing was evaluated by hyperwashing the 0-sample.

5.5 Filter pads and laboratory sheets

Filter pads were made using ash-free filter paper and a Bühner funnel with vacuum pump. The filter papers had to be dried in 105 °C for at least two hours and weighed before using. Two reference samples were made on each sample of reject and accept of each test point. Approximately 200 ml of pulp suspension was weight to be filtrated and ca. 50 - 55 ml of reject. To form filter pads from hyperwashed pulp, ca. 250 g of sample was filtrated. Because brightness for the filter pads of accept pulp was also measured, the samples were dried by vacuum

and temperature for 10 minutes. The reject samples were dried on a hot plate for 10 minutes. The consistency of the samples was defined after standard ISO 638:1978 and ash of dry content after standard ISO 1762:2001.

Laboratory sheets were made using Rapid-Köthen method. The Rapid-Köthen sheet former has a large filter area, ca. 300 cm^2 and with it a very uniform distribution is achieved /43/. Laboratory sheets were made only for accept samples but not hyperwashed samples. Two reference sheets were made of each sample using approx. 250 g of a sample per sheet. The sheets were dried by vacuum and heat.

5.6 Analyzing the visual appearance

ISO-brightness was the only optical property that was analyzed from the filter pads and laboratory sheets. ISO-brightness was measured with Elrepho 2000 following standard ISO 2470:1999. The other measurements to analyze the visual appearance of the samples were counting the dirt specks and ink elimination. Dirt specks were counted from laboratory sheets using a scanner-based image analysis system and the computer program Dot-Counter 4.5. Ink elimination was analyzed also from laboratory sheets with INGEDE Method 10. This method is based on determining the light absorption coefficient K of undeinked and deinked pulp using infrared light (wave-length 700 nm) /44/. It is quantitative analysis of ink elimination during pulping. Ink elimination was measured with Elrepho 2000, the laboratory sheets of 0-sample and 12min.-sample were used for the analyze.

5.7 Calculation of losses

Different kinds of yields and losses are evaluated for the process to see that it is balanced and profitable. For this laboratory flotation total dry content loss and ash loss was calculated after 6 minutes flotation and after 12 minutes of flotation. The losses were calculated as percentages of inflow which this case is the initial values of the full laboratory cell. The calculation of total and ash loss after 6 minutes of flotation was simple but the calculation of total loss and ash loss after 12 minutes

of flotation were more complex because in the calculation the values after the first 6 minutes are taken into account cumulatively. The calculation of ash loss after 12 minutes is a bit more complicated because it takes into account the amount of dry solids content of the reject. The calculations are shown in equations (II), (III), (IV) and (V).

$$Loss_{Total,6min.} = \left(\frac{DC_{R,6min} \cdot V_{R,6min}}{DC_I \cdot V_I} \right) \cdot 100\% \qquad \text{(II)}$$

$$Loss_{Ash,6min} = \left(\frac{A_I - A_{A,6min}}{A_{R,6min} - A_{A,6min}} \right) \cdot 100\% \qquad \text{(III)}$$

$$Loss_{Total,12min} = \left(\frac{DC_{R,12min} \cdot V_{R,12min}}{DC_I \cdot V_I} \right) \cdot 100\% + Loss_{Total,6min} \qquad \text{(IV)}$$

$$Loss_{Ash,12min} = \left(\frac{A_I - A_{A,12min}}{X} \right) \cdot 100\%$$

$$X = \frac{V_{R,6min} \cdot DC_{R,6min} \cdot A_{R,6min} + V_{R,12min} \cdot DC_{R,12min} \cdot A_{R,12min}}{V_{R,6min} \cdot DC_{R,6min} + V_{R,12min} \cdot DC_{R,12min}} - A_{A,12min} \qquad \text{(V)}$$

where $DC_{R,6min}$ is dry solids content of reject after 6 minutes of flotation

$V_{R,6min}$ is volume of reject after 6 minutes of flotation

DC_I is dry solids content of the inflow

V_I is volume of the inflow

A_I is ash content of the inflow

$A_{A,6min}$ is ash content of accept after 6 minutes of flotation

$A_{R,6min}$ is ash content of reject after 6 minutes of flotation

$DC_{R,12min}$ is dry solids content of reject after 12 minutes of flotation

$V_{R,12min}$ is volume of reject after 6 minutes of flotation

$A_{A,12min}$ is ash content of reject after 12 minutes of flotation

X is the nominator in equation V, loss of ash after 12 minutes of flotation.

6 RESULTS AND DISCUSSION

6.1 Brightness compared to total loss

There are considerable variations between the brightness gained with different chemicals used in pulping and flotation. Figure 20 presents the final brightness achieved as well as the dry content losses from flotations. As can be seen, the highest brightness (62.07 %ISO) of this trial is at test point 2 and the lowest (58.25 %ISO) is at test point 18. From table 2 in chapter 4 (Trial plan) can be seen that soap made of animal based fatty acid was used at test point 2 and emulsion 4 at test point 18. The difference between the highest and the lowest brightness is over 3.8 %-units; such a brightness difference would be enough to cause disqualification. A relevant observation is however that the brightness gained with silicone derivatives, test points 5 - 14, were across the board a bit lower than with fatty acid based chemicals excluding emulsion 4. Total dry content losses among the test points vary greatly, from approx. 19 % to 29%. The dry content losses are values after 12 minutes of flotation which are calculated with equation IV presented in chapter 5 (Materials and methods).

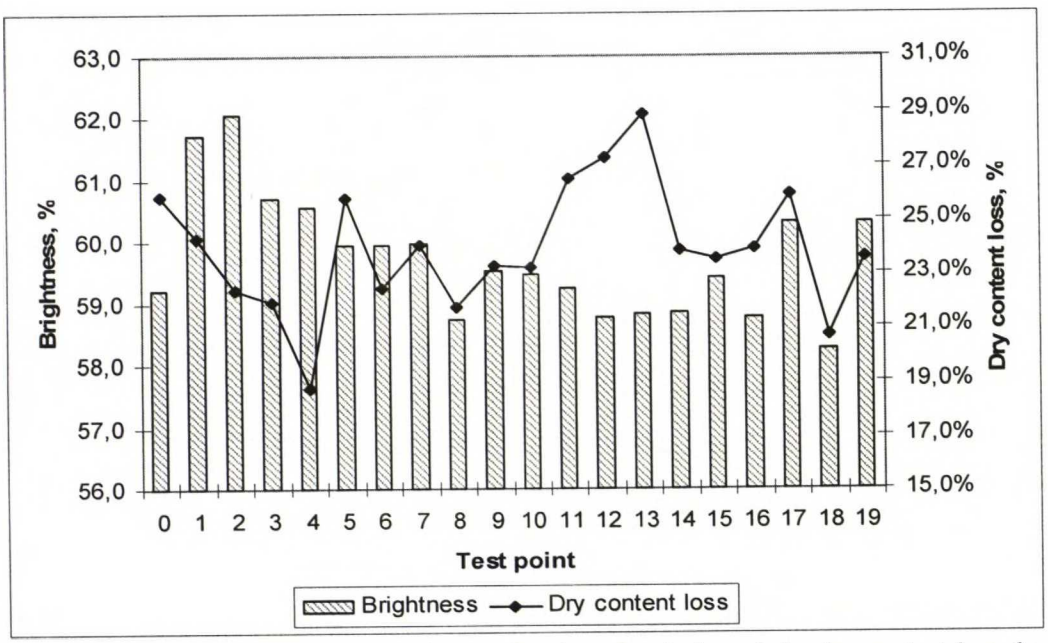

Figure 20. Brightness gained with different flotation chemicals and the dry content loss they caused after 12 minutes of flotation.

Noticeable is that with adding silicone derivative 1 to flotation, test points 7 and 9, higher brightness was gained compared to when the newer modification silicone derivative 2 was added to flotation, test points 8 and 10, though with little higher dry content losses. Peculiar is also that using only pulping chemicals (sodium hydroxide, peroxide and water glass), test point 0, brightness higher than with silicone derivative at test point 8 or with emulsion used at test point 18 can be achieved but with noticeably higher loss.

As presented in the trial plan, table 2, trials to affect pH by adding different amounts of sodium hydroxide and hydrogen peroxide were made, test points 11 - 16. As can be seen in figure 20, when smaller amounts of sodium hydroxide, or none, were dosed, it decreased the final brightness and in most cases increased the dry content loss. The reduction of sodium hydroxide however did not have a significant effect on the pH of the pulp slurry. Sodium hydroxide is added to the pulping process to swell the fibres and so helping to detach ink, it is even said that higher pH saponifies and hydrolyzes some binders of printing inks /15/. Reduced brightness could be due to reduced ink detachment. When a bigger amount of hydrogen peroxide was dosed to affect pH, test point 13, it only increased dry content loss. Acid dissolves calcium carbonate originating from fillers and coating pigments, this is also related to reducing yield /15/.

The target brightness after pre flotation in the deinking process at this mill varies from 56.5 - 57.2 %ISO depending on the grade of paper being produced. The brightness values of pulp slurries of this laboratory trial have been gathered into the table 5. As can be seen from the brightness values gained after 12 minutes of flotation, all the values are above the target values set at the mill. Of course in laboratory flotation the conditions differ greatly from those in the real process and the values gained in laboratory are just indicative but with careful analyze decisions considering the production process can be made.

Table 5. Brightness values of the pulp slurries in laboratory trial.

Brightness			
Test point	0min	6min	12min
Flotation 0	44.96	57.45	59.22
Flotation 1	47.00	59.79	61.73
Flotation 2	46.34	60.19	62.07
Flotation 3	44.68	58.62	60.70
Flotation 4	46.03	58.25	60.57
Flotation 5	46.23	57.67	59.96
Flotation 6	46.23	57.67	59.96
Flotation 7	44.91	57.42	59.98
Flotation 8	46.23	56.03	58.74
Flotation 9	45.95	56.87	59.53
Flotation 10	44.78	56.52	59.48
Flotation 11	45.08	56.77	59.26
Flotation 12	45.40	57.34	58.77
Flotation 13	44.14	56.25	58.83
Flotation 14	44.94	56.98	58.85
Flotation 15	45.35	57.41	59.43
Flotation 16	44.35	56.80	58.76
Flotation 17	45.86	58.82	60.33
Flotation 18	42.96	56.09	58.25
Flotation 19	45.86	58.82	60.33

Based on these trials, if the amount of total dry content loss was set to a constant, not all the test points would achieve the target brightness. This can be seen in figures in Appendix I. The figures show how the brightness and losses of both total and ash develop as the flotation goes on. In these figures has also been marked the brightness that could be achieved with 20 % total dry content loss. Test points 11 - 13 clearly fail in gaining the highest target brightness (57.2 %ISO) after primary flotation set at this mill. At these test points silicone derivative 2 was dosed in pulping and the amount of sodium hydroxide was reduced. Even though the supplier suggests that silicone derivatives are not influenced by pH, at least in the pH range of 7 - 9, it could be concluded that this silicone derivative is more sensitive to the effects of sodium hydroxide in pulping, meaning it perhaps cannot compensate for the absence of sodium hydroxide as well as soap.

Figure 21 illustrates the increase of brightness during flotation. The figure is independent from the variations of initial brightness, so the effectiveness of flotation chemicals can bee seen clearly. The variations of brightness before

flotation are due to variation of raw material. Even though the torn paper pieces were properly mixed the 300 g samples taken still contain different amounts of filler and coating particles as well as fresh and already recycled fibres. If a sample happens to contain more magazine paper aka more fillers, coating particles, chemical fibres it is bound to have higher initial brightness than a sample containing more news print. But the bottom line naturally is that the quality of recycled paper varies daily so with the chemical used in the deinking process should be able to reach acceptable brightness with tolerable losses no matter what the initial brightness is. There are also ways to affect the initial brightness, like sorting the recovered paper and adding more magazine paper to the process.

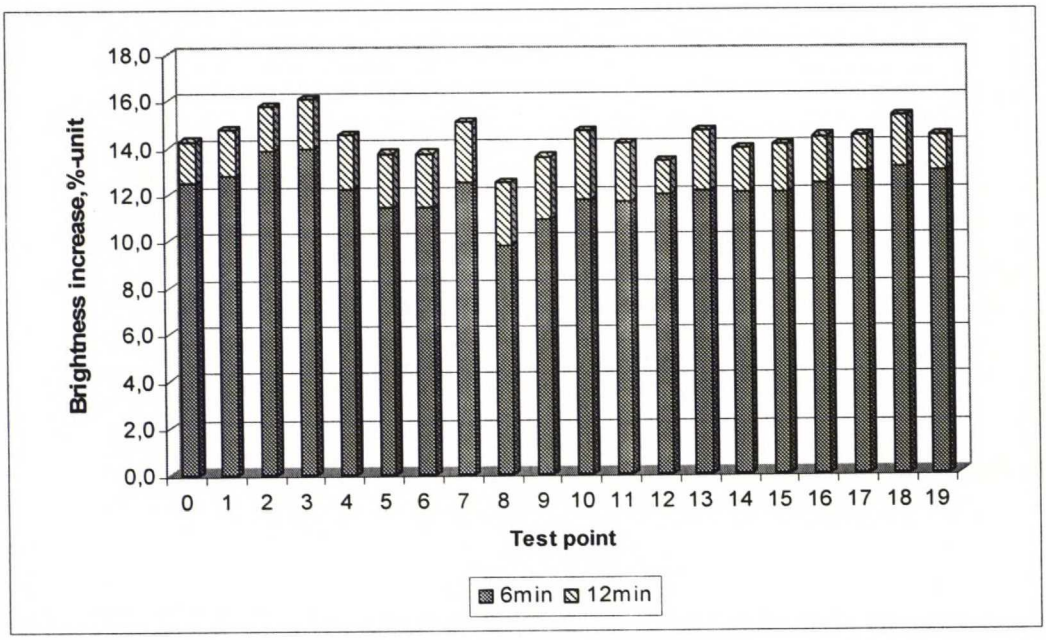

Figure 21. Brightness increase after 6 min. and 12 min. of flotation.

The increase of brightness in figure 21 is on the average approx. 14 percentage units from its initial value during the 12 minute flotation. During the last six minutes the increase in brightness is only few percentage units, the free ink has mostly already been removed during the first six minutes. If the flotation continued, at some point the brightness would actually start to decrease because more and more fillers, coating particles and fines would be removed. It seems that according to these results that point has nearly been reached in these laboratory trials.

In figure 22 can be seen the brightness increase that would have been achieved with 20 % total loss in laboratory trials. The values are counted from the results gained from the laboratory trials so there might be some error especially if the total loss of 20 % have been reached either clearly before or after 6 minutes of flotation.

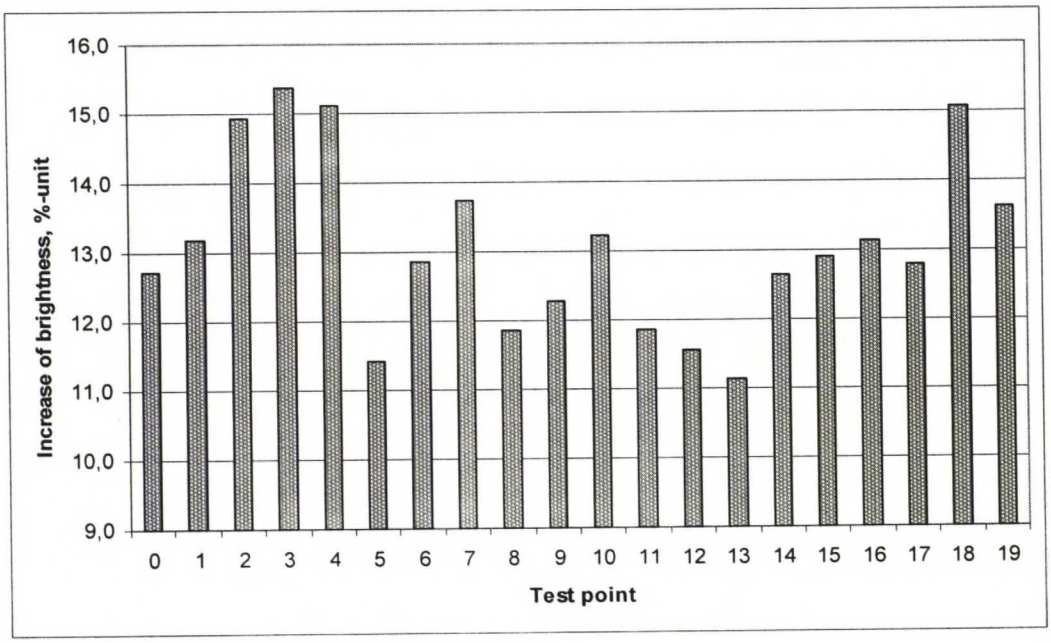

Figure 22. Brightness increase with 20 % total loss.

When compared to the values in figure 21 where the brightness increase is achieved after 12 minutes of flotation no matter how big the loss is, can be seen the limit of 20 % total loss is reached before the 12 minutes flotation time is up, except for test point 4. With the emulsion 2 used in test point 4 the brightness increase would have been higher if the flotation had continued till the limit of 20 % total loss would have been reached. With test points 11 - 13 the limit of 20 % total loss was reached already during the first 6 minutes of flotation. At these test points silicone derivative 2 and smaller amounts of sodium hydroxide or none at all was dosed. Also at test points 14 – 16 either silicone derivative 1 or some soap and silicone derivative 2 was used for pulping or flotation but that the sodium hydroxide was not dose did not have as great an effect. This shows also that the pH has an effect on the function of silicone derivatives, especially on the newer modification.

Figure 23 presents the total brightness increase as well as the total dry content loss. Compared to figure 20, figure 23 is independent of the initial brightness and shows only how much each flotation chemical can increase the brightness of the pulp. Comparing dry content loss to brightness increase gives a better view of the effectiveness of different flotation chemicals than when comparing to final brightness, because this way the variations caused by the paper mixture prepared for these trials do not have as big an effect; theoretically the paper mixture is homogenous.

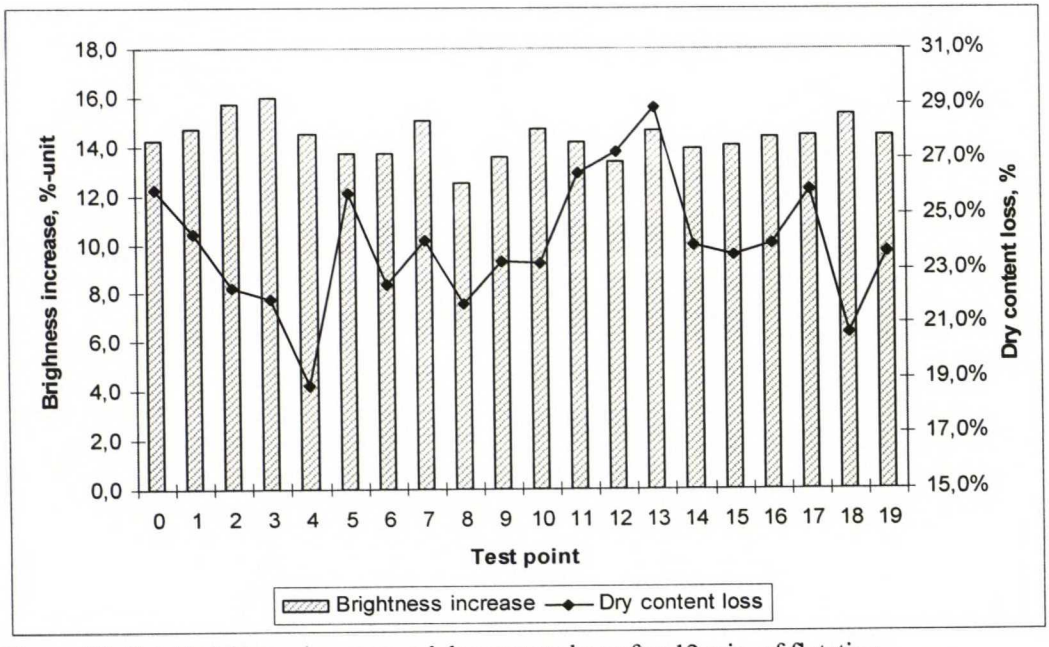

Figure 23. Total brightness increase and dry content loss after 12 min. of flotation.

In figure 23 it can be seen that the highest increase in brightness was achieved at test point 3, from trial plan it can be seen that emulsion 1 was used in pulping and soap 1 was added to flotation. This brightness increase was achieved with one of the lowest dry content loss too. From this figure can also be seen better that the reduction of sodium hydroxide (test points 11 - 16) or the increase of peroxide (test point 13) has not that remarkable an effect on the effectiveness of deinking chemicals. The reduction of sodium hydroxide seems to increase dry content loss when silicone derivative 2 was used (test points 11 - 13). With silicone derivative 1, the reduction of sodium hydroxide does not seem to have such an influence (test point 14). Also when soap 1 is added together with silicone derivative 2, the

reduction of sodium hydroxide had a trivial effect (test points 15 and 16), the dry content loss being only slightly higher. From figure 23 it could be concluded that dry content loss plays a more important role than brightness increase when comparing the superiority of different deinking chemicals in this work.

6.2 Reject and ink elimination

There are big differences between the amounts of reject in different test points as figure 24 shows. The highest final brightness was not achieved with the highest amount of reject. In figure 24 it can also be seen that during the first 6 minutes more reject was formed than during the last 6 minutes. During the first 6 minutes also more ink is removed, that was noticed also in the colour difference of the reject samples.

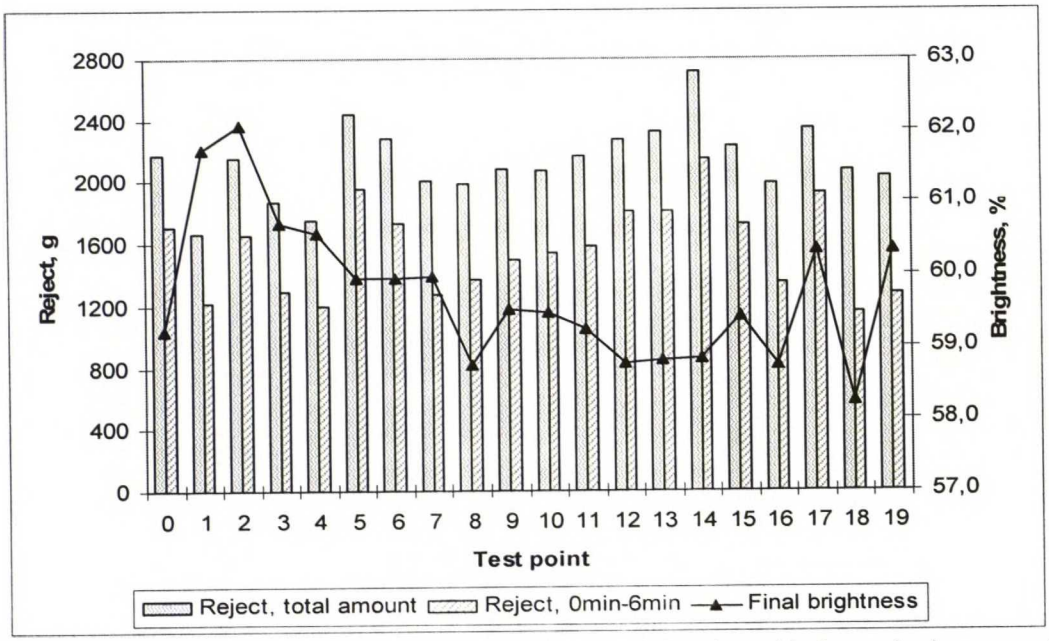

Figure 24. Reject amount in grams after the first 6 min. of flotation with the total reject amount after the 12 min. flotation compared to the final brightness of the accept achieved.

There are also variations in the consistencies of the rejects, which can be seen in figure 25, so a high amount of reject does not have to mean high dry content loss. The consistency of the reject has of course its effects on sludge treatment. It is easier to remove water from already thicker sludge and the amount of water

removed will not be so large. Although there are also limits on how thick the sludge can be so that it can still be handled. If the consistency of the sludge is higher than 4 - 5 % it is too thick to go through pumps from storage tanks to sludge treatment. If the consistency is under 2 % the limiting factor for sludge treatment is its volume capacity. If the sludge is weak, there is usually going more sludge into the treatment and more water to be removed.

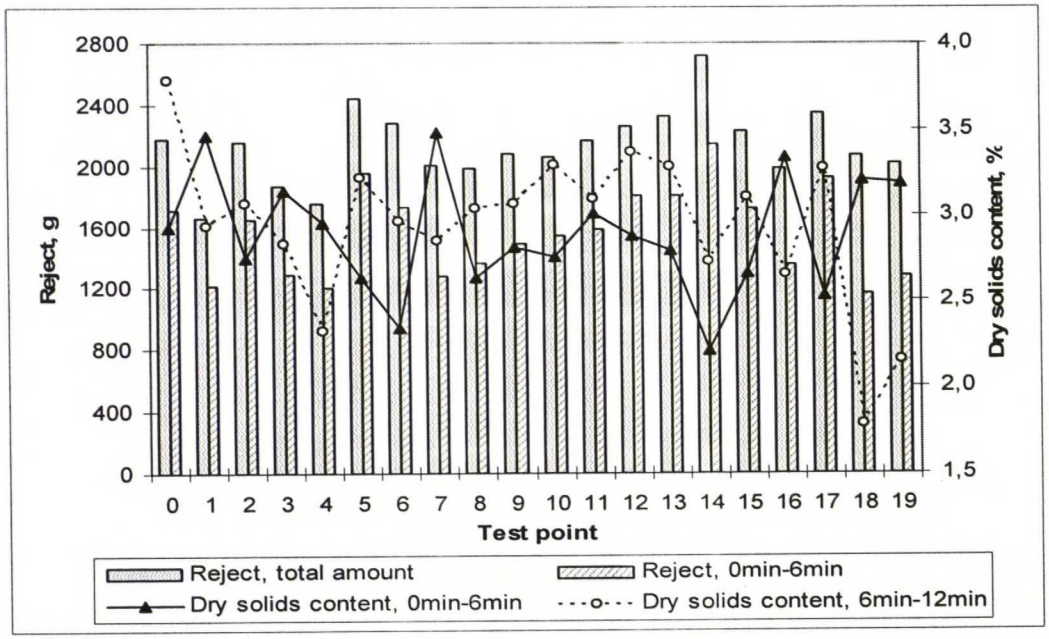

Figure 25. Reject amount in grams after the first 6 min. of flotation with the total reject amount after the 12 min. flotation and dry solid contents for reject after first and second 6 min. of flotation respectfully.

Figure 26 shows not only the variations in reject amounts but also the ash content of the rejects, ash content in reject from the first six minutes and reject from the last six minutes alike are presented. More ash is removed during the first six minutes, ink likewise, but still quite a lot of ash is removed also in the latter six minutes flotation period.

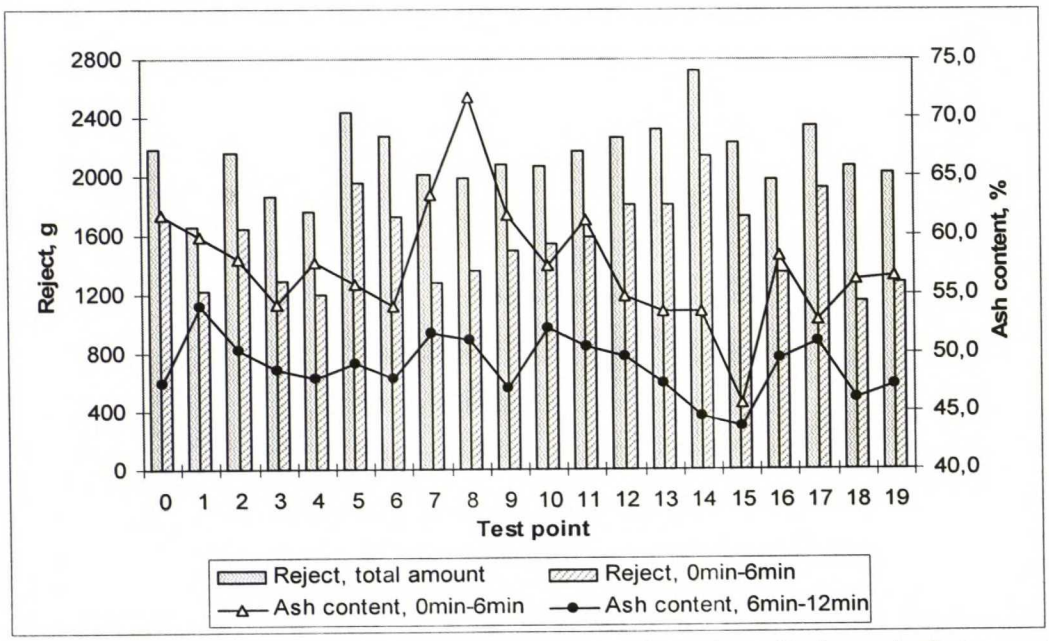

Figure 26. Reject amount in grams after the first 6 min. of flotation with the total reject amount after the 12 min. flotation and ash contents for reject after first and 6 min. of flotation respectfully.

In these trials how the flotation cell was filled had a big effect on the amount of reject. With another technique the amounts would probably be lower. Also the variation might balance out a little. As explained in the chapter 5 (Materials and methods) in these trials the flotation cell was filled first and then aeration was started after the shortage due to sample-taking was compensated for. This causes variation in reject amounts because the volume of the overflow caused by aeration was different with different chemicals. Some chemicals had a larger volume overflow because they failed producing decent layer of froth in the beginning when the aeration was started and air coming from the bottom of the cell pushed more liquid over, thus the dry solids content of the reject turned out to be low although the amount of reject was high. With the other technique the aeration would be started right after the sample was taken and the shortage filled only after that till the overflow was adequate, the reject amounts would be reduced and the variations were not so big. Then also the effect of chemicals on dry content loss would better be seen.

Ink elimination is really an indicative measure because, as can be noticed from figure 27, with high ink elimination the brightness can still be low or higher brightness can be gained with lower ink elimination. This can at the most show the variations in raw material. Ink elimination and amount of reject do not seem to have any obvious correlation.

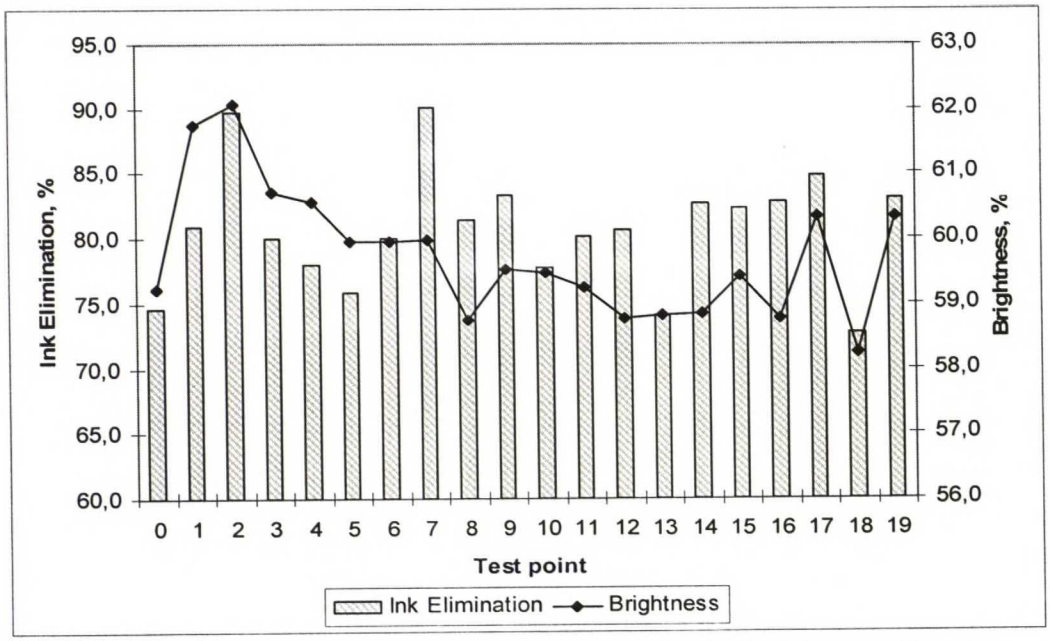

Figure 27. Ink elimination after 12 min. of flotation compared to final brightness achieved.

6.3 pH of the pulp slurry and water hardness of fresh water

The pH was measured from each pulp slurry sample of each test point. The figures can be found in Appendix II. The pH does not seem to be a significant factor for brightness. The variations of pH level out as the flotation goes on. As mentioned earlier, the attempts to affect pH were not successful, probably because of the buffer effect of sodium silicate. The reduction on the dosage of sodium hydroxide and increased amount of hydrogen peroxide had a mild effect on pH but a more obvious effect on fibre loss.

Water hardness does not seem to have an effect on brightness as can be concluded from figure 28. That means that there was enough calcium ions present for the

soaps to work properly. The values of water hardness and pH of fresh water are gathered in a table presented in Appendix III.

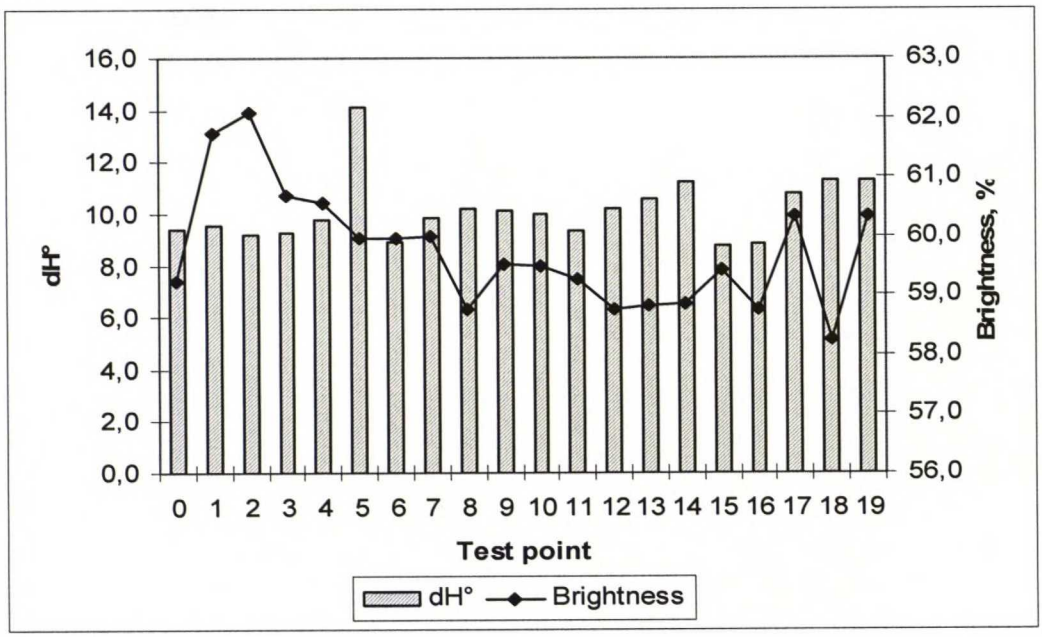

Figure 28. Hardness of the freshwater used in deinking compared to the final brightness after total 12 min. flotation.

The silicone derivatives are independent of water hardness /28/. Because fatty acids require calcium ions in order to function, the water hardness has to be at a certain level. The required minimum water hardness, 5 - 12 °dH, depends on the sources used /15, 30, 45/. One °dH corresponds to 17.8 ppm $CaCO_3$ /15, p. 249/. The sodium soap reacts with the calcium ions in water forming calcium soap according to the following chemical equation /15, p. 248/:

$$2\,\mathrm{RCOONa} + \mathrm{Ca(OH)_2} \rightarrow (\mathrm{RCOO})_2\mathrm{Ca} + 2\,\mathrm{NaOH} \qquad (3)$$

6.4 Effects of hyperwash

The brightness values of hyperwashed pulps are presented in figures 29 and 30. In figure 29 are the brightness values of 0-samples before and after hyperwashing, and in figure 30 are those of 12min.-sample. As can be seen in both figures, the values at times vary greatly.

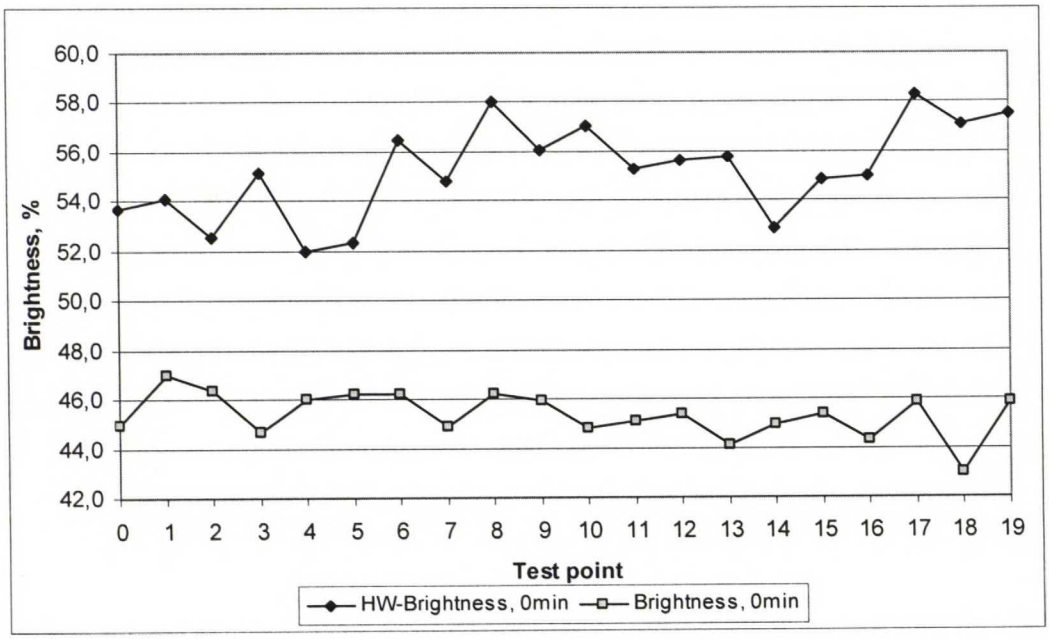

Figure 29. Brightness of non-flotated pulp before and after hypwerwashing.

The brightness variations appearing in figure 29 for non-hyperwashed samples can be explained by variations of quality and type of recycled paper used as raw material because there is always a possibility, although the pieces of paper were properly mixed, that the samples have contained various amounts of fillers and different printing inks.

The ink particles that can still be found in the sample after hyperwashing are nondetached ink particles. The conditions and machinery used in pulping as well as the raw material have a strong influence on the detaching behaviour of ink particles from the fibres. That is why the brightness variations with hyperwashed 0-samples are even greater than with non-hyperwashed. But in this case that is not the only reason. The consistency variations shown in Appendix IV seem to have an influence on the brightness variations. With lower consistency the brightness was higher and that might mean the filter paper is showing through the sample and giving higher brightness. The ash consistencies also showed in Appendix IV can not explain the brightness variations. There happened an error of judgement while the samples were prepared after the discordant laboratory instructions, this would explain why the filter papers could show through. Unfortunately this error was discovered a little bit too late.

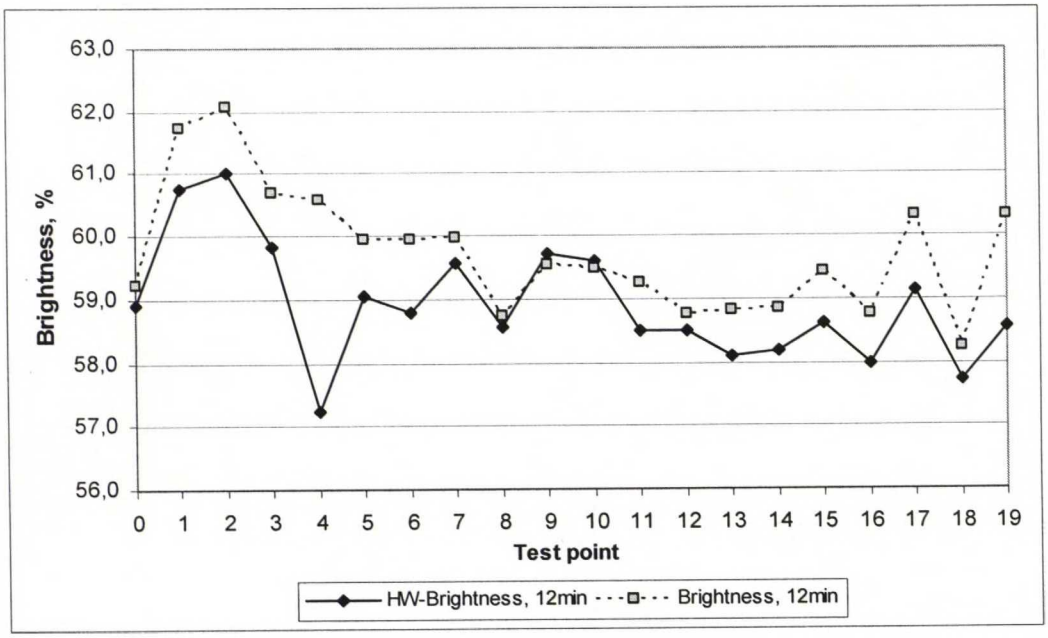

Figure 30. Final brightness before and after hyperwashing.

The brightness variations between the 12min.-samples are expected because different amounts of ink and fillers as well as fines are removed during flotation. Comparing the final brightness with the brightness of hyperwashed 12min.-sample presented in figure 30, the flotations have been very successful. As long as the difference of brightness between hyperwashed and non-hyperwashed pulp is equal to or smaller than 2 percentage units it can be said that the deinking has been successful. This rule applies when the brightness of hyperwashed pulp is greater than that for the non-hyperwashed pulp. In this case the brightness of the non-hyperwashed pulp is higher or almost equal in every test point which means that the detached ink particles have been removed efficiently in flotation and the hyperwashing is only removing particles increasing brightness, those being fillers, coating particles and fines. Also a longer flotation time would only decrease yield and brightness.

From figures found in Appendix IV it can be concluded that variations in dry solids content and ash content do not have that strong an impact on brightness values for final brightness and hyperwashed 12min.-sample.

7 MILL SCALE TRIAL RUN

7.1 Trial plan

The procedure for the mill scale trial run was primarily planned by the people supplying the chemical and approved by the people responsible for the production of deinking plant. The plan was executed in collaboration. The purpose of this trial run was to replace the soap in deinking process with silicone derivative. The initial setup of the process was that soap was being dosed to pulping, flotation, secondary flotation, post flotation and secondary post flotation. The dosage amounts and places are gathered in table 6 /38/. The amounts are percentage of the amount of bone dry pulp in the process.

Table 6. The dosage points and amounts of soap before trial.

Dosage point	Dosage amount (%)
Pulper 1	0,1
Pulper 2	0,1
Feed to the Flotation Line 1&2	0,13
Feed to the Flotation Line 3	0,13
Feed to the Secondary Flotation	process-controlled, 0 - 0.2 l/s
Feed to the Post Flotation Line 1	0,05
Feed to the Post Flotation Line 2	0,05
Feed to the Secondary Post Flotation	process-controlled, 0 - 0.15 l/s

The plan was to replace the soap in the process with the silicone derivative step by step, by starting to dose silicone derivative first and then reduce the amount of soap until it would no longer be dosed. The silicone derivative used was Nopcoflot EGA 3050. One possibility of the target amounts and dosing points of silicone derivative are presented in table 7 /38/.

Table 7. The dosage point and possible amounts of silicone derivative.

Dosage point	Dosage amount (%)
Pulper 1	-
Pulper 2	-
Feed to the Flotation Line 1&2	~ 0,02
Feed to the Flotation Line 3	~ 0,02
Feed to the Secondary Flotation	soap, process-controlled, 0 - 0.2 l/s
Feed to the Post Flotation Line 1	~ 0,005 (optional)
Feed to the Post Flotation Line 2	~ 0,005 (optional)
Feed to the Secondary Post Flotation	soap, process-controlled, 0 - 0.15 l/s

7.2 Execution

The dosing of silicone derivative was started into flotation line 1 with the amount of 0.02 %, the amount of soap was reduced step by step till null. The same was done to flotation lines 2 and 3. After that the dosing of soap to the pulping, both pulpers, was reduced and finished. The dosage of silicone derivative to the flotation lines was set to 0.015 %. Finally the dosage of soap into the post flotation was replaced by silicone derivative with the dosage amount of 0.005 %. There were a few trials before that to try to finish the dosing of soap to post flotation but they failed because too much froth was produced and it was too stable. Ever since there was just silicone derivative in the process, the problem with froth over-production started to increase and because the froth was stable it did not break that easily and the sludge tanks overflowed. Because the dry solids content of the froth was lower than when using soap, it was necessary to increase the overflow from the flotation to maintain acceptable brightness which also led to overflow of the sludge tanks. The problem of froth stability was tried to solve with defrother but in the end that was just a temporary solution. The sludge treatment could no longer handle the increased amount of weak sludge cause by the increased overflow from the flotation because of that the overflow of the sludge tanks was no longer in control. Also the brightness dropped because the contaminants did not remove from the circulation. Finally after about a month of trial run the soap was returned to the system except for pulping. The progress of the trial run can be seen in figure 31. There the dry content of the overflow of

secondary flotation of each three cell has been presented as a function of time. Also the main events are being plotted.

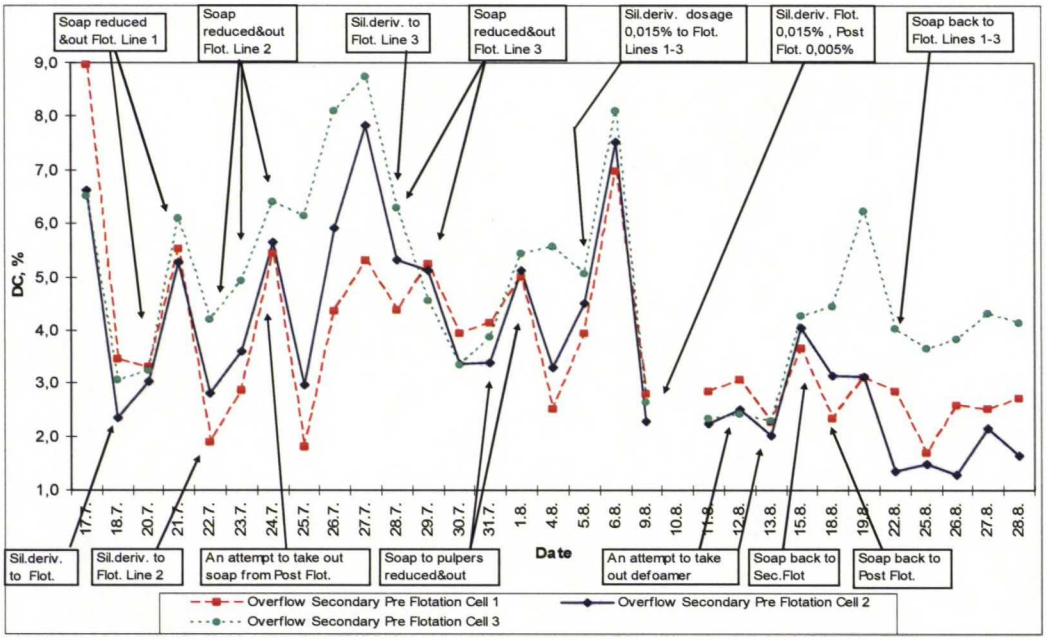

Figure 31. The dry solids content of overflow from each three flotation cell in secondary pre flotation and the progress of the trial run.

7.3 Measurements

The trial run lasted approximately five weeks during which almost every day samples were taken. There were 18 samples and the measurements were done from filtrated pads. The measuring points and the measurements for each point are gathered in table 8. The IDM in the table means an on-line measuring instrument and FS stands for fine screening. Quantifying the overflow from secondary flotation was done with the help of a rectangular bucket capacity of 14 litres and a stopwatch. The sample was then poured into another bucket which was weighed. The width of the rectangular bucket was compared to the width of the flotation cell and thus the total overflow could be calculated. Considering the technique of this measurement, it can cause some error to the results.

Table 8. Samples from the process and the measurements done for each sample.

Measuring point	Measurement					
	Flow rate	Dry content	pH	Ash	Brightness	Brightness HW
Outflow Storage Chest Pre Flotation Line 1	IDM	x	x	x	x	-
Outflow Storage Chest Pre Flotation Line 2	IDM	x	x	x	x	-
Outflow Storage Chest Pre Flotation Line 3	IDM	x	x	x	x	-
Inflow Pre Flotation Line 1 (after Mixing Pump)	IDM	x	-	x	x	-
Inflow Pre Flotation Line 2 (after Mixing Pump)	IDM	x	-	x	x	-
Inflow Pre Flotation Line 3 (after Mixing Pump)	IDM	x	-	x	x	-
Accept Pre Flotation Line 1	Calculation IDM Accept + Reject FS	x	-	x	x	x
Accept Pre Flotation Line 2		x	-	x	x	x
Accept Pre Flotation Line 3		x	-	x	x	x
Reject Pre Flotation Line 3	-	x	-	x	x	-
Inflow Secondary Pre Flotation	IDM	x	-	x	x	-
Overflow Secondary Pre Flotation Cell 1	Quantify	x	-	x	x	-
Overflow Secondary Pre Flotation Cell 2	Quantify	x	-	x	x	-
Overflow Secondary Pre Flotation Cell 3	Quantify	x	-	x	x	-
Accept Secondary Pre Flotation	IDM	x	-	x	x	-
Outlet to Sludge Tank 1	-	x	-	x	x	-
Clear Filtrate 1	IDM	x	x	-	-	-
Cloudy Filtrate 1	Calculation	x	x	-	-	-

When silicone derivative was dosed also in post flotation, a few more measuring points came along. These added measuring points and measurements are gathered in table 9.

Table 9. Samples from the post flotation process and the measurements done for each sample.

Measuring point	Measurement					
	Flow rate	Dry content	pH	Ash	Brightness	Brightness HW
Accept Post Flotation Line 1	Calculation	x	-	x	x	x
Accept Post Flotation Line 2		x	-	x	x	x
Accept Secondary Post Flotation	IDM	x	-	x	x	-
Inflow Secondary Post Flotation	IDM	x	-	x	x	-
Overflow Secondary Post Flotation Cell 1	Quantify	x	-	x	x	-
Overflow Secondary Post Flotation Cell 2	Quantify	x	-	x	x	-
Inflow Post Flotation Line 1	IDM	x	-	x	x	-
Inflow Post Flotation Line 2	IDM	x	-	x	x	-

7.4 Results and discussion

As a consequence of many measuring points and the duration of the trial run, there is so much material that only the most important results are covered here. As can be seen in figure 31 presented earlier the dry content of the overflow from secondary pre flotation varies greatly during the trial run. This implies that the process is not stable which is understandable because of the many changes but the variations when returning back to soap dosing are not that big. The process was not able to stabilize when using silicone derivative as flotation chemical.

In figures 32, 33 and 34 the overflow from secondary pre flotation cells is presented as both volume flow and mass flow for each cell respectively. The mass flow is presented as dry solids content and was unfortunately not quantified from the very beginning. For cell 1 the volume flow commences to grow as the silicone derivative is added to flotation line 1. This implies that overflow has to be greater to sustain a certain brightness level. Although the mass flow grows as the volume flow grows they do not grow in the same proportions. When compared to dry solids content in figure 31, can be seen that often dry solids content decreases as the volume flow increases so the froth formed is weaker, because of that the mass flow does not grow as fast.

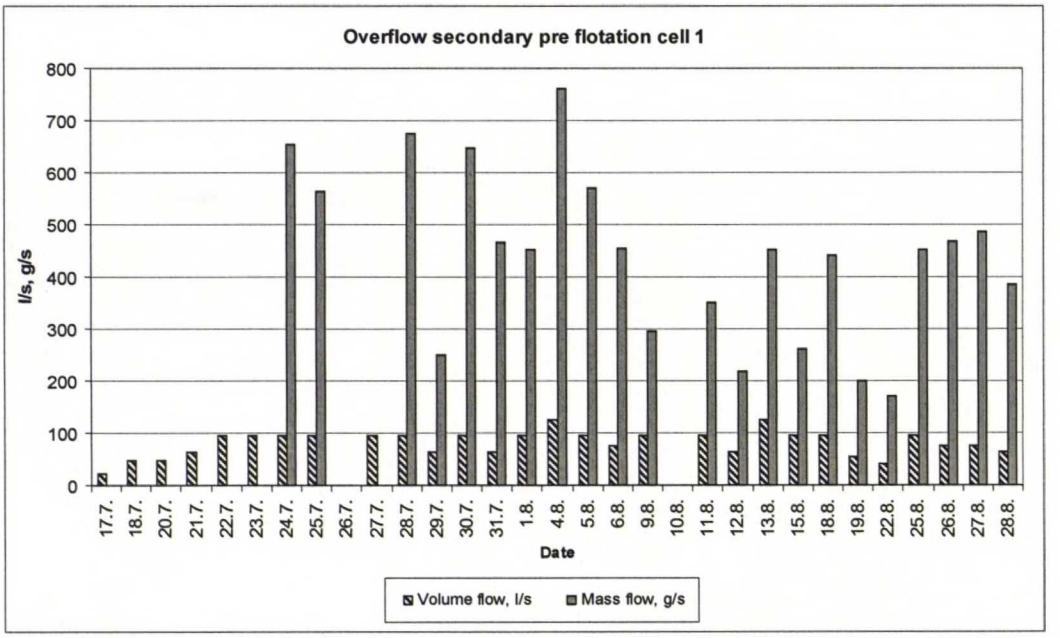

Figure 32. The volume and mass overflow of pre flotation cell 1, mass flow quantified as dry solids content.

The function of EcoCell can clearly be seen in figures 32, 33 and 34. When the dosing of silicone derivative is started, it can actually be observed only in secondary pre flotation cell 1. As the amount of silicone derivative increases in the process more variations can also be found in cells 2 and 3of the secondary pre flotation, for example on July 28th the dosing of the silicone derivative was started to the 3rd and last line for pre flotation.

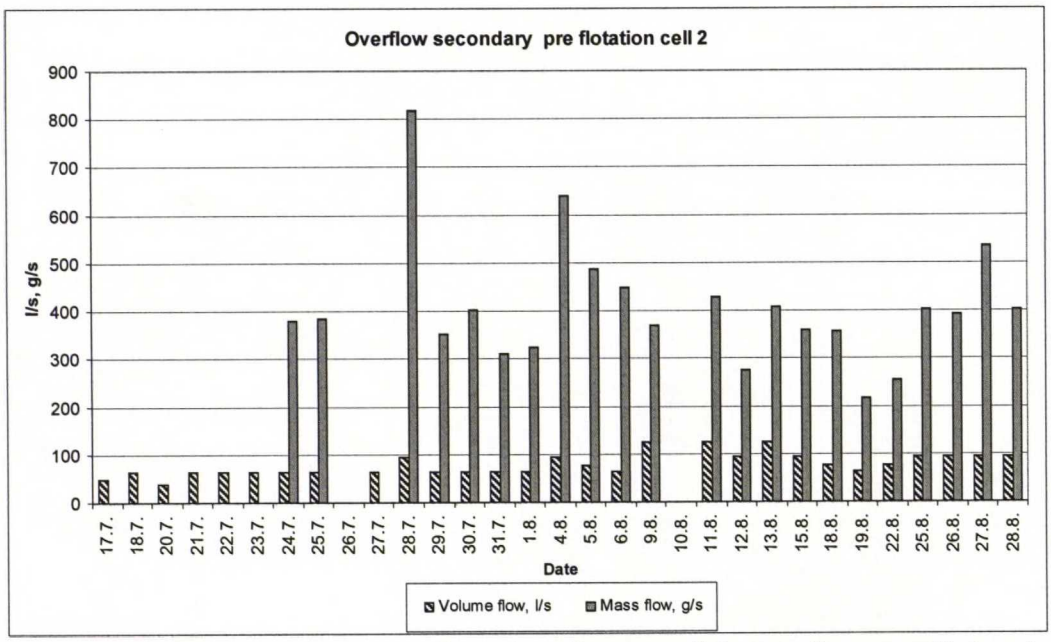

Figure 33. The volume and mass overflow of pre flotation cell 2, mass flow quantified as dry solids content.

The problems with the sludge over-production started when silicone derivative was dosed also into the post flotation. This occurs also in pre flotation and can best be seen in secondary pre flotation cell 3 in figure 34; both volume and mass overflow increase radically because the brightness of the accept has dropped thus more overflow is going to the secondary flotation and the flotation cell 3 of the secondary pre flotation is the last one of the cells and from there the froth goes as reject to the sludge tanks. The purpose of secondary flotation is to reduce loss by collecting back to the process the fibres lost in flotation as much as possible. But the target is to maintain also the brightness approximately at the same level as the inflow to the flotation has so being last in line the secondary pre flotation cell 3 is where this brightness can still be gained. Also in this case the reason for increased volume and mass flow from secondary pre flotation is that the whole secondary flotation system was overloaded because of the highly increased overflow from the flotation.

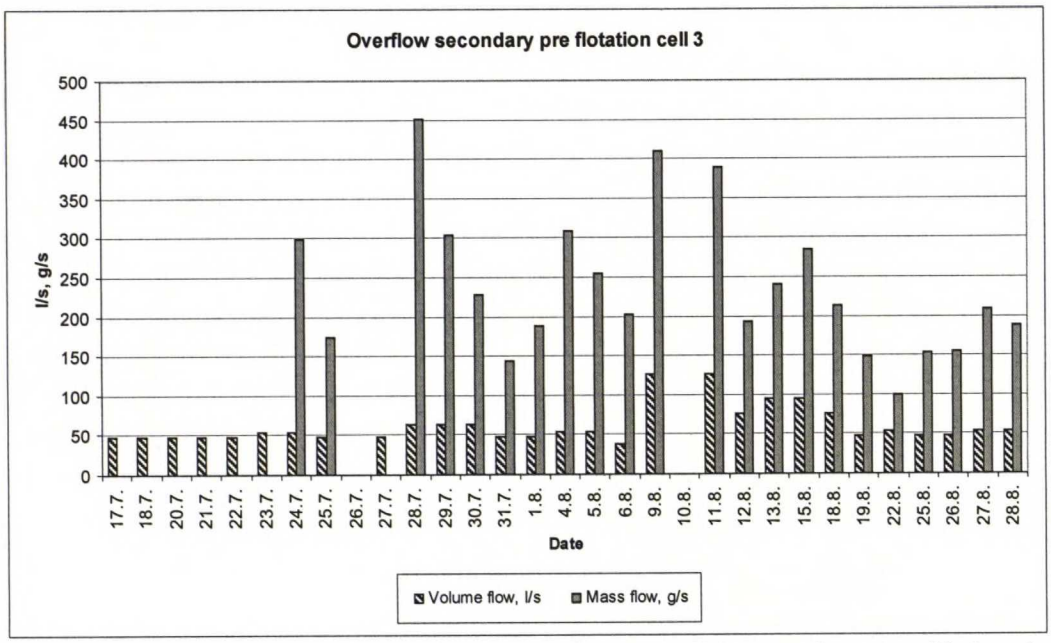

Figure 34. The volume and mass overflow of pre flotation cell 3, mass flow quantified as dry solids content.

The dry solids content and the ash content of the overflow from secondary pre flotation are shown respectively in the figures in Appendix V. For cells 1 and 2 the ash content in the overflow is higher during the trial run than when changed back to soap dosing. Then also the dry content of the overflows drops and the variations settle down. For cell 3 the ash content in the overflow is higher than for cells one and two, so is dry content. But then again, cell 3 is the last cell in the row of secondary pre flotation and there is also the last possibility to remove ink and dirt specks from the process. The problem with froth can be seen in every figure as a drop in dry solids content (9.8.).

The brightness of the accept from pre flotation line 1 - 3 is shown in figure 35. There has also been plotted a line of the minimum target value of brightness after pre flotation just to compare what has been reached during the trial run. The values are daily measured values from the shift laboratory so that brightness values after the trial run as well can be observed. In figure 35 has also been marked when the soap was brought back into the process as well as the point of shutdown.

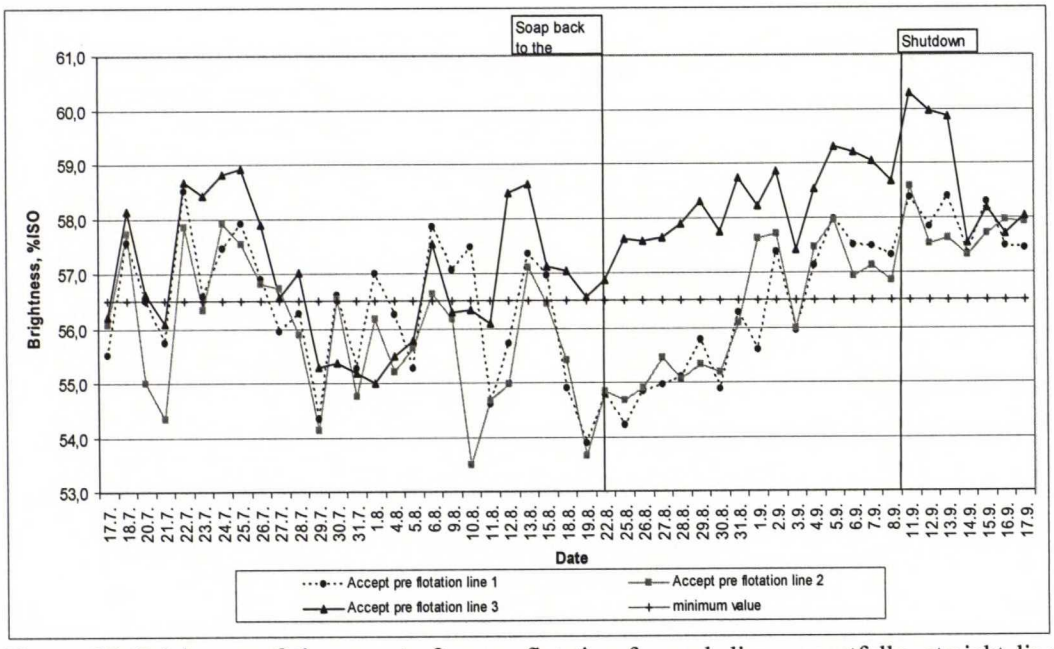

Figure 35. Brightness of the accept after pre flotation for each line respectfully, straight line represents so called minimum target value for brightness after pre flotation.

It seems that when silicone derivative is added for line 1 the accept brightness of line 1 and 2 increases for a moment (18.-20.7.). The same happens when the silicone derivative is added for line 2 (22.-23.7.). The brightness of line 3 increases as the silicone derivative is added to the process but as more silicone derivative is added the brightness starts to decrease. After only silicone derivative is added to the pre flotation lines (23.7.) the variations of the accept brightness start to get bigger for each line. This could be explained by varying dosing amounts of bleaching chemicals, peroxide and dithionite. The variations in brightness are tended to compensate by dosing different amounts of bleaching chemicals; when brightness acceptable bleaching chemicals are not needed and when the brightness decreases it is tried to bring back by bleaching. In this case the decreased brightness is compensated by increased amounts of bleaching chemicals and as the acceptable brightness is reached the dosing amounts of bleaching chemicals can be reduced thus the brightness drops again, hence the fluctuations in brightness. The froth problems appearing after soap is no longer dosed at any stage in the process can be seen as a brightness drop in each line (9.-10.8.). After that the dosing of defrother is started and it seems to help for line 3 with the EcoCell but the other two lines with CF-Cells have still difficulties in

reaching good enough brightness level. When soap is brought back to the secondary pre flotation the brightness of line three drops at first, while for the other lines it increases (15.8.). The soap is brought back to the pre flotation at August 22nd (22.8.) but there are still so many ink particles accumulated in the process that the acceptable brightness for line 1 and 2 is actually reached after shutdown when the flotation cells are washed thoroughly. In figure 35 can be seen also that the brightness starts to increase as soon as soap is dosed into the process. After the shutdown the fluctuations in brightness for lines 1 and 2 starts to even out.

The ash content and the brightness for the accept of each pre flotation line are displayed in Appendix VI. At the beginning of the trial the ash content for lines 1 and 2 stay quite stable. Then the ash content suddenly declines as the third line is taken out of use (30.7.). The production of the deinking mill was already reduced because the flash dryer also out of use, paper machine could not use all the pulp produced by deinking mill and the storage towers were filling. Then the production of the deinking mill was still reduced by running down pre flotation line 3. As the production is decreased the consistency of the inflow to flotation is also decreased. Because of the selectivity of the flotation process and chemicals more ash goes to the secondary flotation and is removed from the process because secondary flotation removes always approximately the constant amount of ash from the process. After that the ash content starts to increase, while a little drop can be noticed as the froth problems emerge. When soap dosing is commenced again the brightness seems to decrease as the ash content increases. Usually fillers and pigments are added to the paper to increase brightness. Perhaps in this case the flotation was unable to remove ink particles as well as fillers and pigment particles and the bleaching agents could not compensate the brightness drop caused by increased amount of remained ink particles. For over half the duration of the trial the accept brightness for lines 1 and 2 was under the minimum target value as can be seen in figure 35. What comes to the flotation line 3, there is much more variation in the ash content during the whole trial than for the other lines. But the brightness stays most of the time above the minimum target. It seems also

that there is no correlation between brightness and ash content of the accept pulp from pre flotation line 3. This could probably be explained with how the flotation cells are controlled. The CF-Cells of pre flotation lines 1 and 2 are controlled with constant mass and volume inflow whereas the EcoCell of line 3 is not so when variations in the process are done, the effect can be seen in flotation line 3. As during the trial run there were a lot of changes done, could this cause that the fluctuations in brightness and ash content of the accept from line 3 are not in correlation.

The brightness after hyperwashing for each line respectively is shown in figures in Appendix VII. As can be seen in these figures, line 3 is the only flotation line that succeeds in gaining the brightness that can be gained because, excluding a few exception, the difference between brightness of the accept and hyperwashed pulp is under 2 percent units. For lines 1 and 2 this is not the case on several days especially after the amount of silicone derivative increases in the process. The situation gets even worse for each line for a few days when the dosing of soap is started again (14.8.) before showing any improvements. This only supports the conclusion that during the trail run the ink is not totally removed from the process but accumulated in the flotation circulation.

Figure 36 presents increase of brightness during pre flotation for each line. At the beginning of the trial run there are lot of variations between the lines but towards the end line 3 seems to increase brightness the most. For line 3 also the brightness of the access appears to follow the trend of how the brightness increases, for the other two lines the trend is not as clear. And even though the increase of brightness is relatively high during the problems with froth (9.8.-13.8.) it is not enough to reach the desired brightness level. This indicates also that the ink accumulates in the process and is not removed successfully.

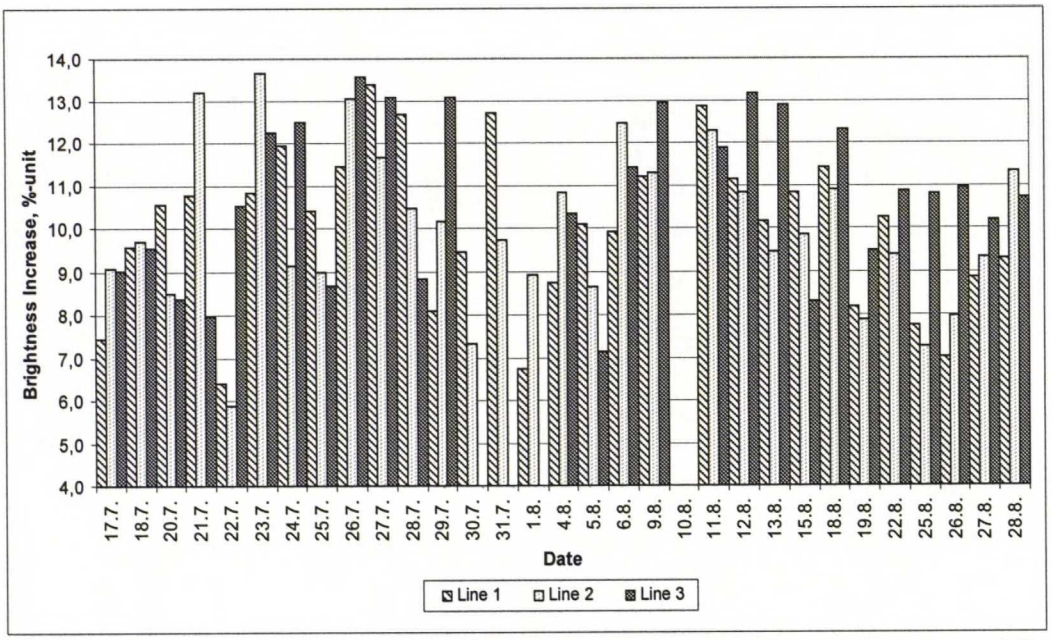

Figure 36. Brightness increase in percentage units of pre flotation for each three lines respectfully.

Also the brightness of secondary pre flotation inflow and accept was measured and the results are shown in figure 37. The importance of secondary flotation can be observed in this figure. Its purpose is to minimize loss, that is, collect as many of the fibres which have overflowed from the primary flotation. Here the brightness increases approximately by over 10 units of %ISO; this implies that quite an amount of ink is still removed from the fibres and fillers returning to the primary flotation. The purpose of secondary flotation is also gain the brightness of the pulp going back to the flotation to the same level as the inflow to the flotation cells has coming from the screening stage.

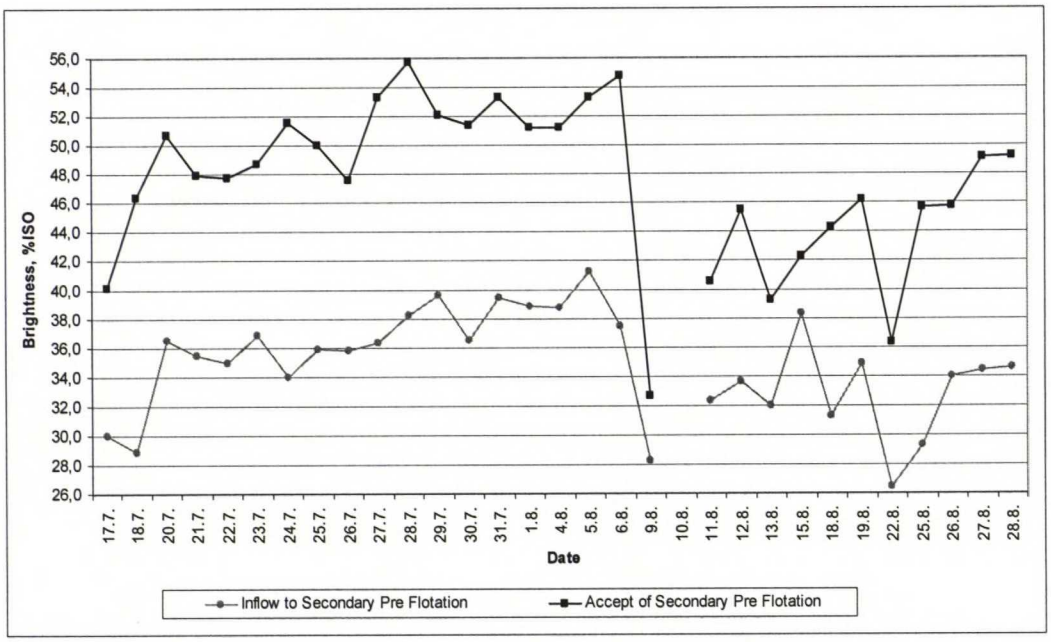

Figure 37. The brightness of inflow and accept of the secondary pre flotation.

As the trial run is started the brightness of the inflow increases, this implies that although the secondary flotation is still working normally the primary flotation is no longer removing as much ink as it used to; soap was still added to secondary flotation. As an outcome of removing the soap from the process the brightness of inflow and accept plunged (9.8.). After that the fluctuation grows and the increase of brightness diminishes. The fluctuations do not even out as soon as dosing of soap into the secondary flotations is restarted. Soap is lastly added back into the primary flotation (22.8.) and only just after that the process of secondary pre flotation seems to balance.

Total loss of pre flotation in figure 38 is presented as loss of dry solids content. It is calculated from the mass flow that goes into the pre flotation and reject flow from the secondary pre flotation which is actually defined using values of inflow and accept flow of secondary pre flotation. The values used for calculation of dry content loss in pre flotation are defined from the samples taken that day so it tells actually just the loss at the moment as the samples were taken. But it gives us an indication of the trend of dry content loss in pre flotation.

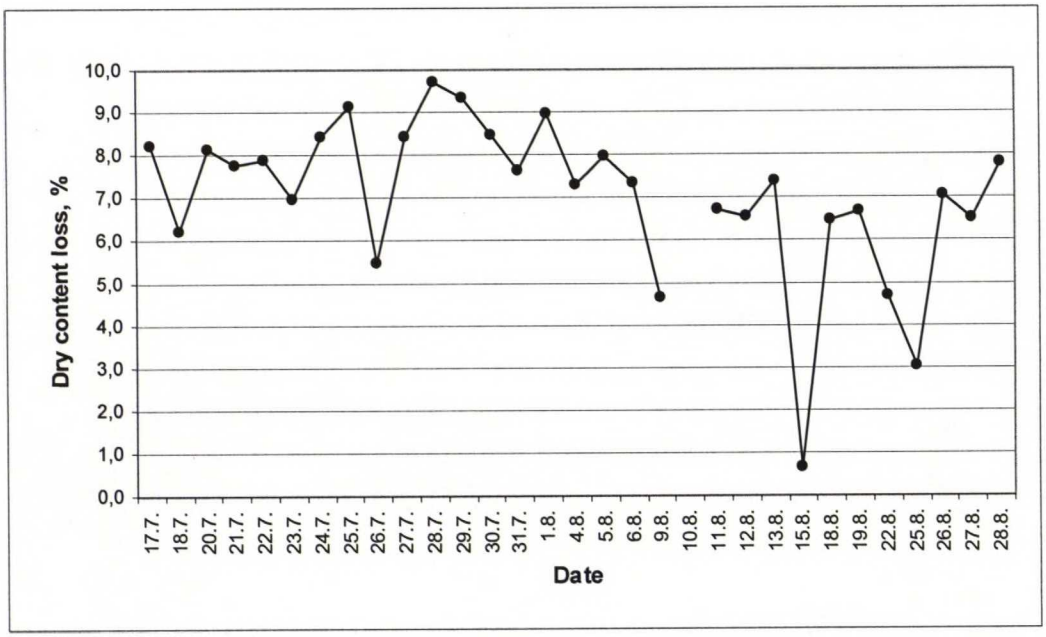

Figure 38. Total dry content loss over the pre flotation.

The curve of total loss of pre flotation shows a little upward trend at the beginning of the trial run. After starting to add silicone derivate to line 3 in pre flotation (28.8) the curve turns downwards. That is not necessarily a good thing because it can also mean that more ink stays in the process. E.g. on 9th of August as there were a lot of problems with too much froth, the loss of pre flotation is rather low but the quality of the deinked pulp was not acceptable at the time. Even bigger variations can be seen as the dosing of soap was started (15.8.). Bigger dosing amounts of soap for pre flotation were needed than before starting the trial run to gain the required quality for the deinked pulp. As soap was brought back into the process, there was a short trial to run the pulping without soap that is why more soap had to be dosed into the flotation.

The production of the deinking mill and the total loss over the process can be seen in figure 39. The values in this figure are daily averages of bone dry values which are calculated using air dry and bone dry on-line values. It is good to bear in mind that averages are no absolute values but they can give us an idea, a trend, about how the production and total loss develop during the trial run. The value of production is reported as tons per day and the value of total loss as percentages of the production.

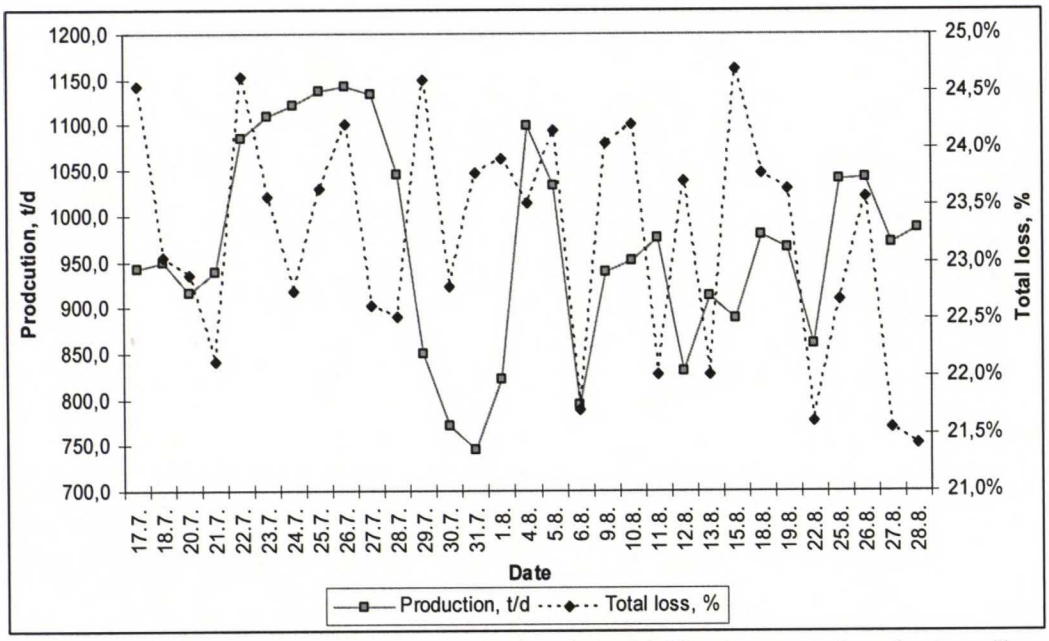

Figure 39. Total loss of bone dry material over the whole deinking process and production of bone dry pulp per day.

In figure 39 there are two major pits of production. The drop in production taking place on the turn of the month (30.7.-1.8.) was caused by shut down of one of the pre flotation lines because of lower demand for deinked pulp on the paper machine and the flash dryer was also out of order. The drop on 6th of August (6.8.) was also caused by lowered production; on the next day there were a shutdown at the deinking and as a preparation the production was decreased. Other fluctuation in production are more caused by the diminishing amount of recycled paper in the summer time and the production had to follow the production of the paper machine, there were so to say no more paper recourses to produce deinked pulp for sale. The fluctuations in total loss are not exceptional from the normal production.

No results of the post flotation are discussed here because the silicone derivative was dosed to post flotation only for seven days of which samples were taken only on three days. No trends can be seen because of lack of results. The conclusions leading to the decision to quit the trial run were drawn from the problems appearing throughout the process.

8 CONCLUSIONS

The market conditions today force us to think where savings can be made to maintain or even increase profit. The weak exchange rate of the U.S. dollar compared to the Euro has ensured that the markets are unfavourable to European production. As the energy prices increase more attention is paid to biodiesel. Fatty acid being raw material for both biodiesel and soap used in deinking, it is obvious that the chemical costs for deinking increase. New products to compete with fatty acid based soap in deinking are being invented and tested; some of them are already in use at some mills.

Several different chemicals used for ink removal in flotation deinking and their combinations were tested in laboratory scale trials. In general the results show why fatty acid based soaps have a dominant position in deinking. But the differences were quite small in some cases so the chance to replace fatty acid with other product exists, and in this case the substitute product tested was a silicone derivative. Different combinations of chemicals and their dosing amounts were examined. In general the results gained with fatty acid based products were better than those gained with silicone derivative based chemicals. But the inferiority of silicone derivatives was only marginal, especially with silicone derivative 1, and the potential lies in cost savings. According to these trials at least, reducing sodium hydroxide in pulping is not an option; as the results show it only adversely affects the end result by increasing dry content loss and decreasing ink removal efficiency. Neutral process conditions were not reached in these trials, when tried the quality of the pulp suffered. Perhaps the approach to neutral deinking conditions was not designed correctly. The lack of sodium hydroxide was not compensated by any other chemical that could have helped with the ink detachment the way sodium hydroxide does. That is probably why the brightness of the pulp remained low. And to get the pH to neutral level other chemical should be used, chemicals which are neutral itself.

In table 10 has been gathered condensed information of which test point had a good influence on the properties listed also in table 10. The price did not cover any storing or heating costs; just the purchase price was considered and compared to the demanded dosing amount. As can be seen the chemicals giving the best quality for the deinked pulp (test points 2 - 4) are also the most expensive and thus not really an option because the savings gained with better quality are not nearly enough to cover the cost. And the other way around, although it would be very cost effective to deink using just the necessary pulping chemicals without any soap or other flotation chemicals (test point 0) the quality of the deinked pulp would be so poor that it would not be worth to produce.

Table 10. Properties affected by the deinking chemicals and the nature of the effect.

Property	Brightness	Brightness increase	Reject amount	Dry content loss	Ash loss	Ink elimination	Price
Test point							
0	-	+	-	-	+	-	++
1	+	+	+	-	-	+	-
2	+	+	-	+	+	+	-
3	+	+	+	+	+	+	--
4	+	+	+	+	-	-	--
5	+	-	-	-	-	-	-/+
6	+	-	-	+	-	+	-/+
7	+	+	-/+	-	+	+	-/+
8	-	-	+	+	-	+	-/+
9	+	-	-/+	+	-	+	+
10	-	+	-/+	+	-/+	-	+
11	-	+	-	-	-/+	+	-/+
12	-	-	-	-	+	+	+
13	-	+	-	-	-/+	-	-
14	-	-	--	-/+	+	+	+
15	-	+	-	+	+	+	-
16	-	+	+	-/+	+	+	+
17	+	+	-	-	+	+	
18	-	+	-/+	+	-	-	
19	+	+	-/+	+	+	+	

The amount of reject considered in table 10 was air dry. The amount of reject in general does not play a significant role because the amount can be easily influenced by filling the laboratory cell differently. Thereby also the variations would partially balance out. Although in the real process the surfaces of the flotation cells are controlled, in these laboratory trials it was not wanted to do so

that the true effect of different chemicals tested on foaming and reject could better be seen. When evaluating the influence of different chemicals on flotation result, crucial properties are loss of dry content and ash as well as brightness increase because then the initial brightness does not have decisive influence. The final brightness is still worth taking into account because no matter what the quality of recycled paper varies and the deinking chemicals should still be able to achieve acceptable results. The best result in these trials when especially price is considered is gained at test point 7 with a dosing amount of 0.02 % silicone derivative 1 added into the flotation.

Although according to the laboratory trials better results were gained with silicone derivative 1 than silicone derivative 2 still the decision to do the mill scale trial with the latter was made. This was because silicone derivative 2 is a newer product and thus more advanced with better qualities, it works in larger temperature variation range as its predecessor and thus the process has bigger limits for temperature fluctuations.

The mill scale trial run was started with dosing silicone derivative into the process and step by step reducing the dosing of soap until only silicone derivative was added. The trial run proceeded quite nicely at the beginning as soap was replaced with silicone derivative in all three pre flotation lines and soap dosing into the pulping was stopped. Problems really started when the soap in the post flotation was replaced by silicone derivative and at the same time the dosing of soap into both secondary flotations was stopped. As a consequence the brightness of the deinked pulp dropped and consumption of hydrogen peroxide and sodium dithionite increased in trying to maintain the brightness. Also the amount of froth overflowing from secondary flotation increased and the froth was so stable it did not break on its way to the sludge containers; the stability of the froth and the increased overflow from process caused the sludge containers to overflow. The production of forth was over 10 %, at times even close to 20 %, grater than in normal conditions so the capacity of the sludge treatment was reached rather quickly. The trial run had to be terminated because the process was no longer

under control and thus unable to produce acceptable quality. When the soap dosing was restarted the problems with the froth disappeared eventually but the battle with the low brightness continued till shutdown during which efficient washing was carried out.

On the basis of the results of the mill scale trial the supplier suggested that silicone derivative would replace soap only in pre flotation and soap would be left out from pulping. This suggestion would bring in two thirds of the savings that could be reached with a target plan of using only silicone derivative. But the soap to the secondary flotation must be left untouched because soap has an effect that silicone derivatives do not possess. Soap makes the froth thicker which causes slightly higher dry content loss but the froth is easier to handle and the volume of reject stays more constant. At the end of the mill scale trial run some other possibilities to save chemical costs were tried out. When soap was brought back to the system it was not dosed in pulping as it was before trial. This would save even more that the suggestion of the supplier of silicone derivative. Heating costs would not have to be considered because soap would be dosed in either way. Unfortunately this does not seem to be an option because the results were not those desired. Perhaps there was still too much ink left over from the trial with silicone derivative. Based on the results from laboratory studies a mill scale trial run using the older modification of silicone derivative could accomplish the desired result. This would also create even bigger savings than any of the options presented above because the product would be cheaper than its successor. Actually a trial run using silicone derivative 1 is going to be launched while this paper is being finished.

For further laboratory scale trials it might be interesting to study some other chemicals used for ink removal in deinking like some surfactants that have been recently developed. Also some more attention could be paid to the effects of water glass in pulping. At least in these laboratory trials the amount of water glass dosed (0.8 %) was considerably higher compared to what is dosed in the real process (0.31 %).

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List of Appendixes

Appendix I The final brightness that would be achieved in laboratory trials when the loss of dry solids content is set to constant 20 %.

Appendix II Laboratory trial run, effect of pH to final brightness.

Appendix III Results of the measurements made for fresh water.

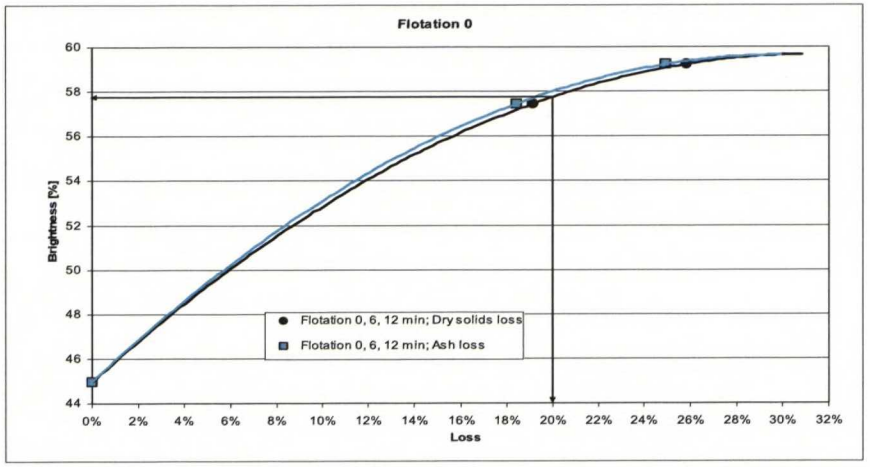
Appendix IV Dry solids content, ash content and brightness of the hyperwashed pulp of non-flotated pulp and after 12 min. flotation in laboratory trials.

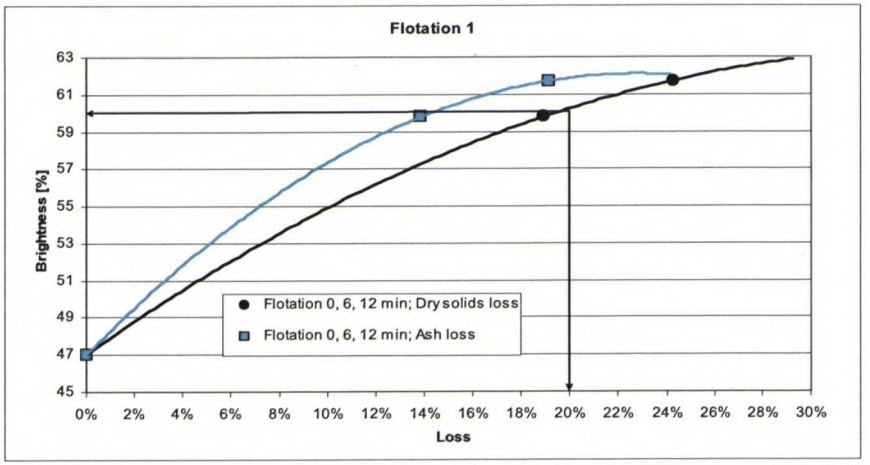
Appendix V Dry solids and ash content of overflow form each secondary pre flotation cell in mill scale trial run.

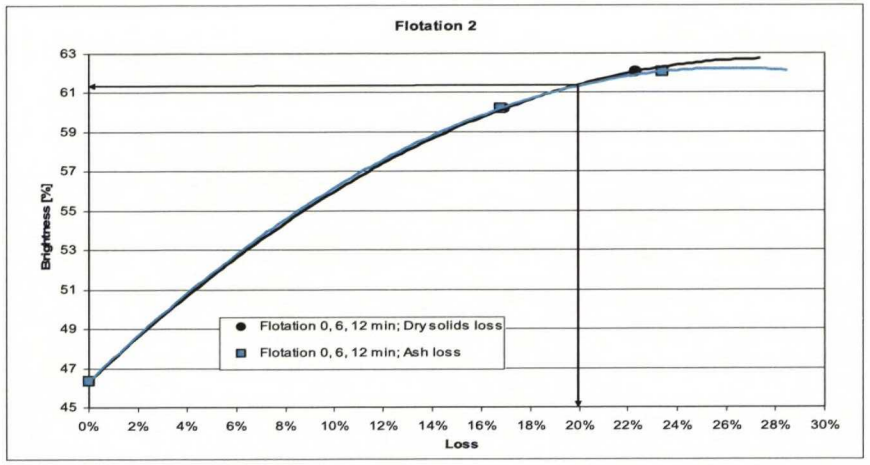
Appendix VI Brightness of the accept and its ash content for each pre flotation line in mill scale trial run.

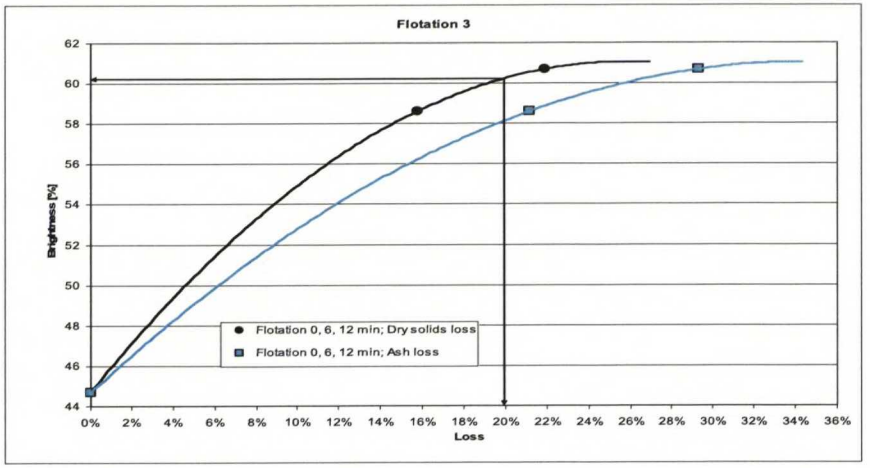
Appendix VII Brightness of the accept compared to hyperwashed brightness of each pre flotation line in mill scale trial run.

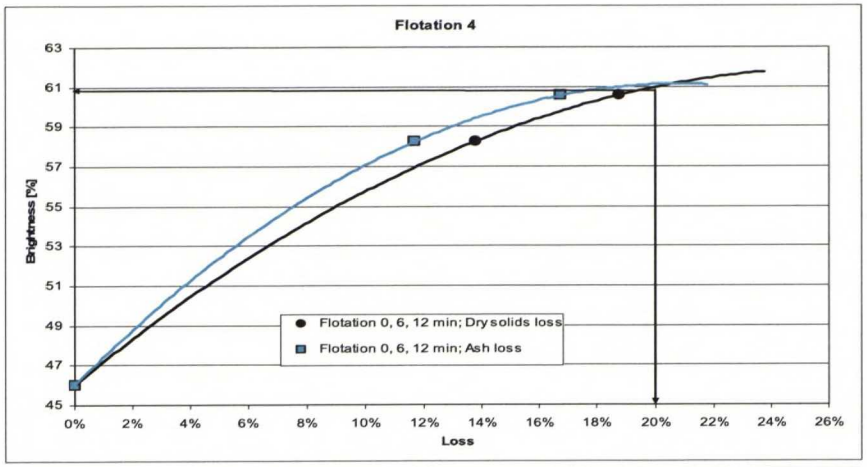
The final brightness that would be achieved in laboratory trials when the loss of dry solids content is set to constant 20 %.

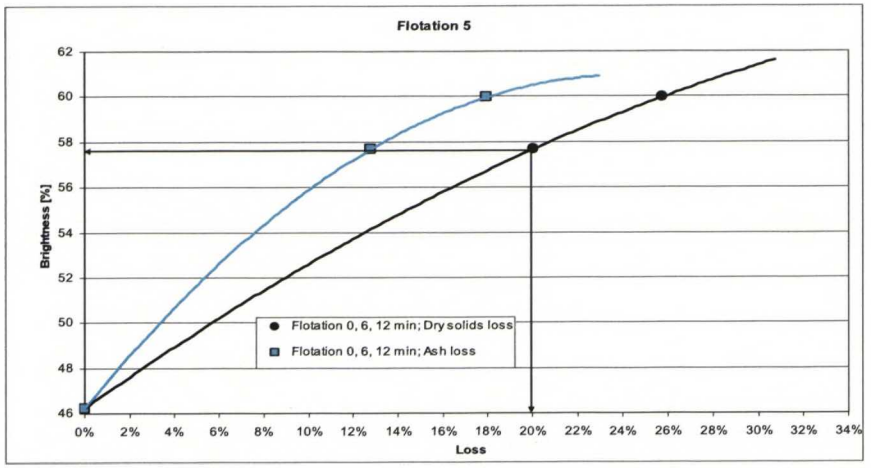


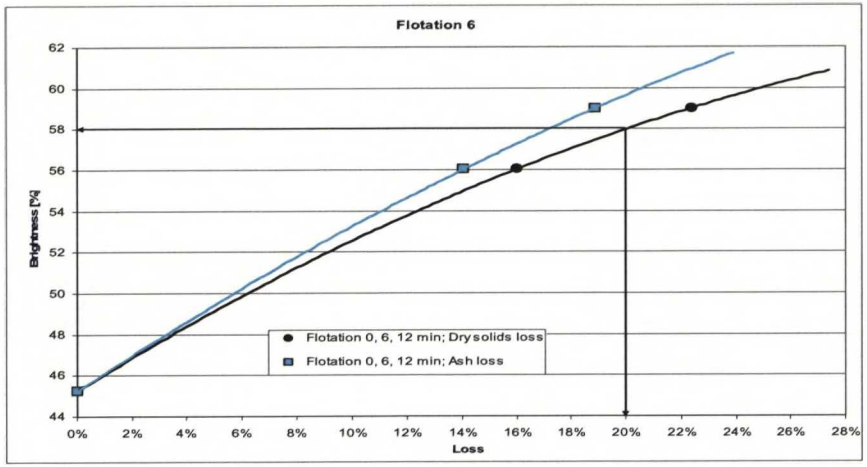


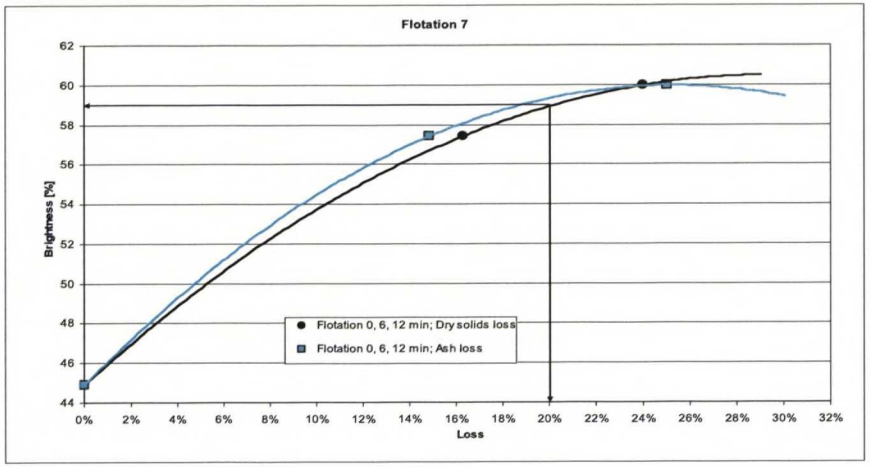


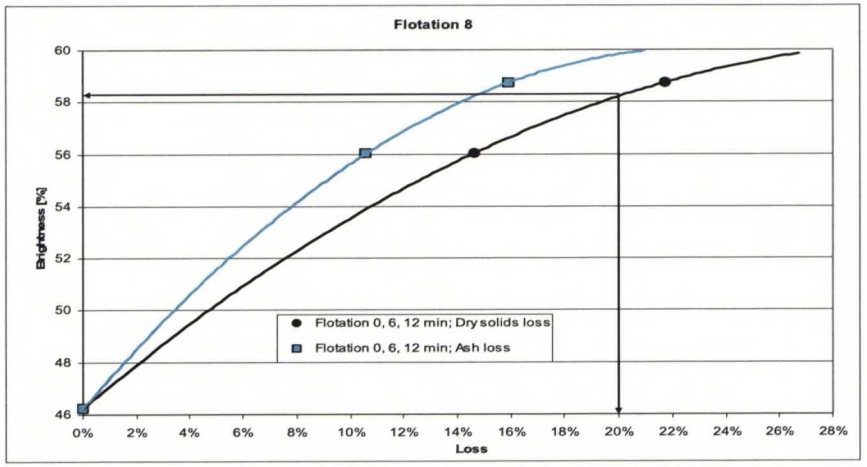


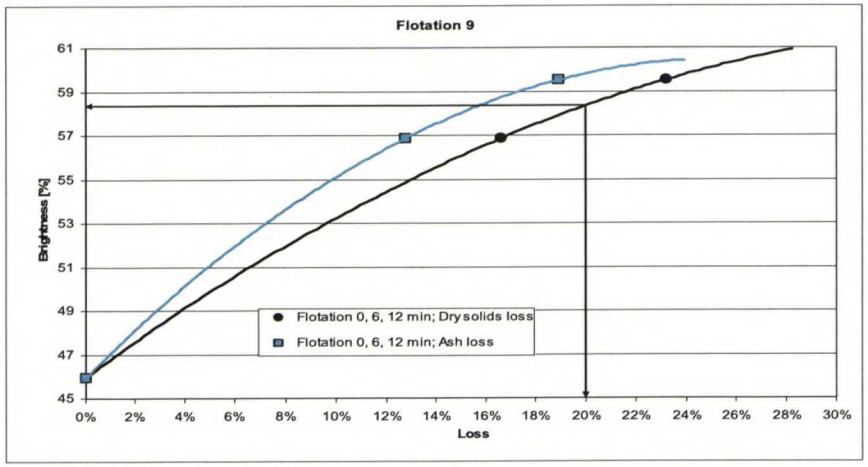

Flotation 4
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

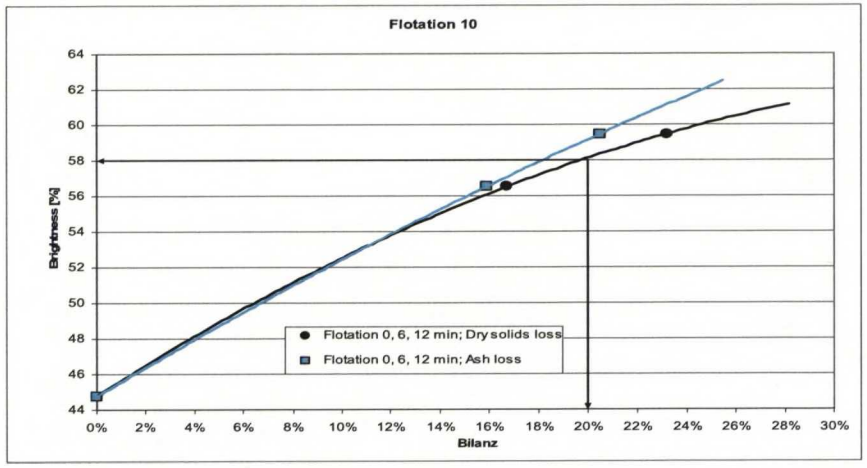

Flotation 5
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

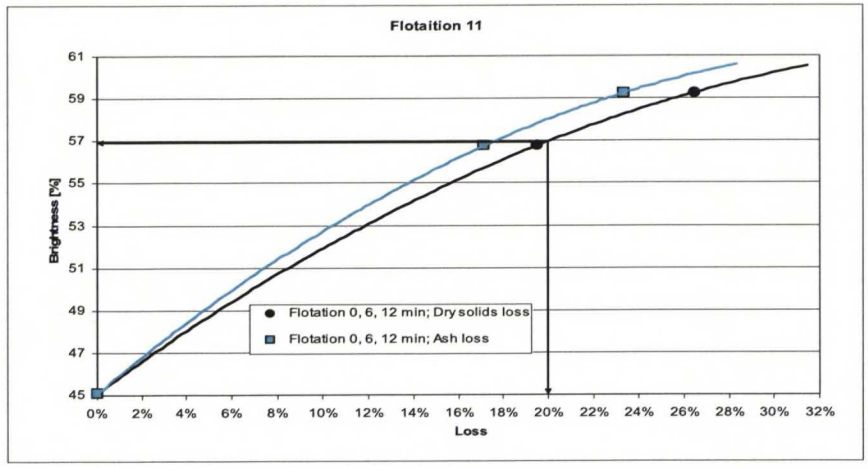

Flotation 6
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

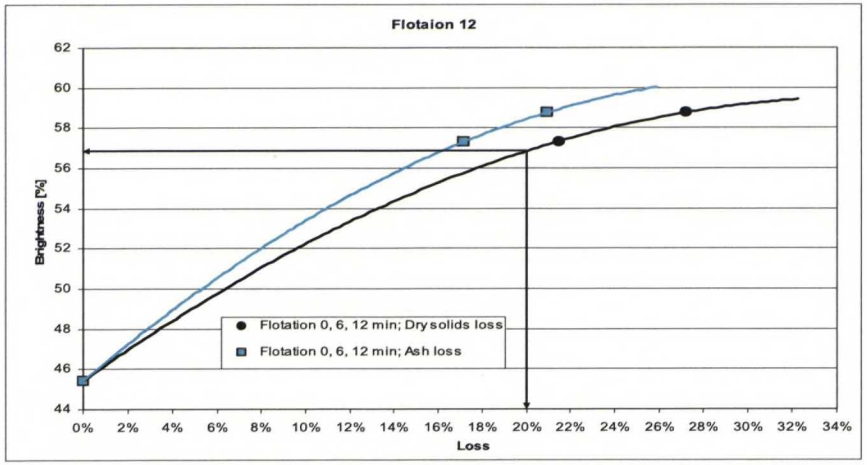

Flotation 7
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

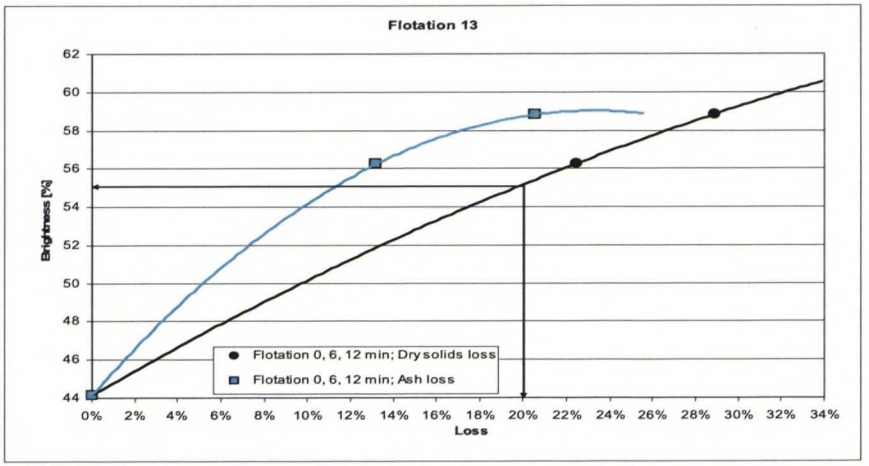

Flotation 8
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

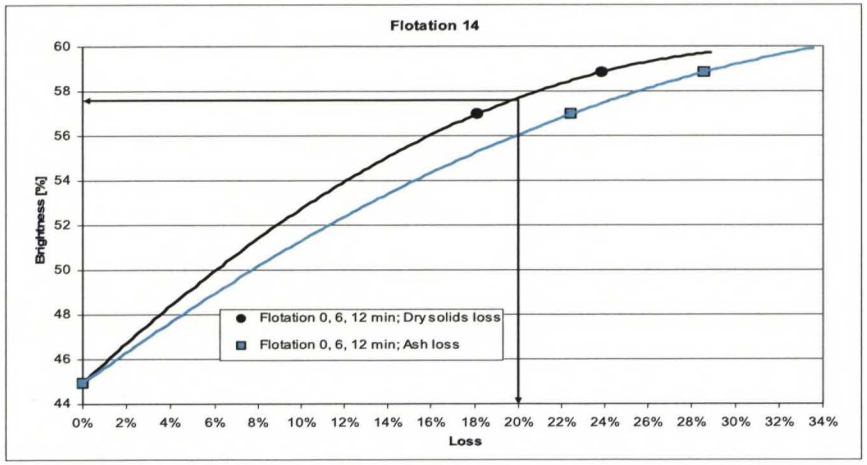

Flotation 9
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

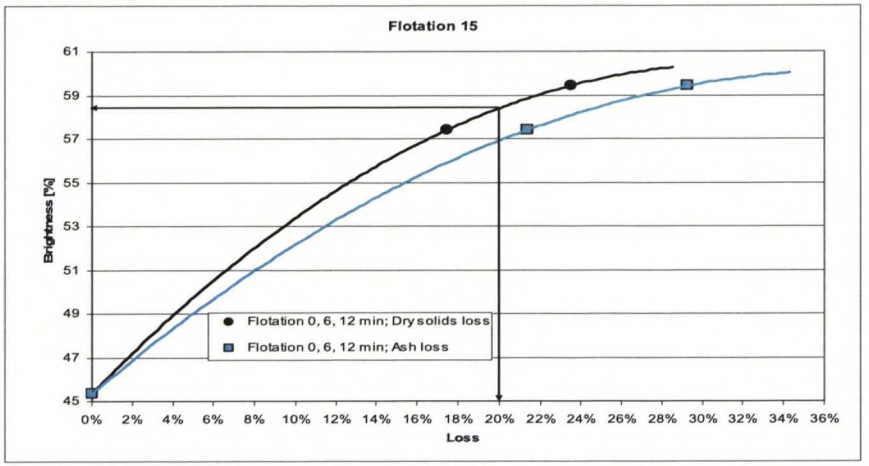

Flotation 10
Brightness [%]
Bilanz
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

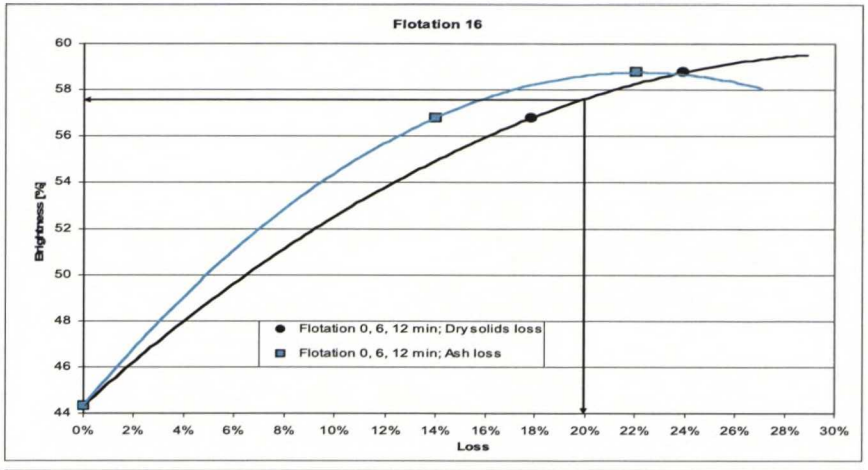

Flotaition 11
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

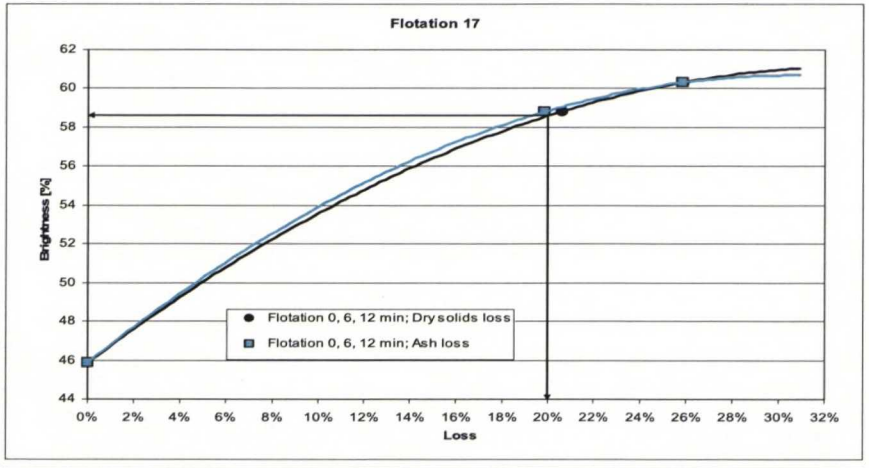

Flotaion 12
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

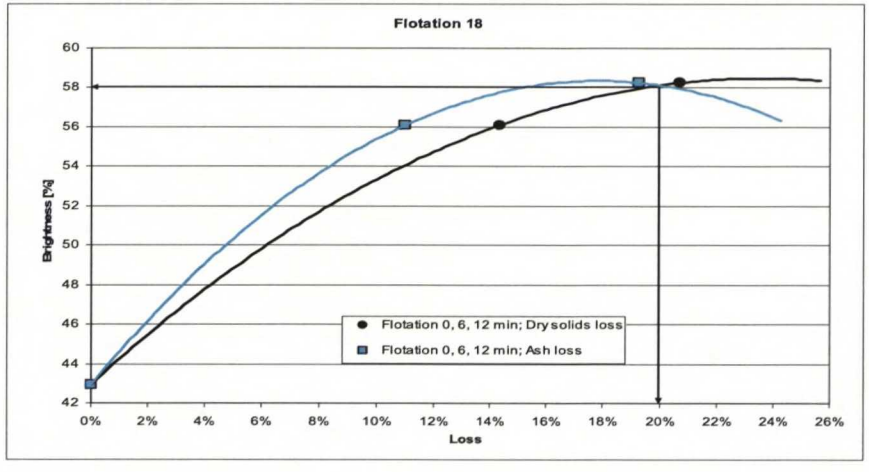

Flotation 13
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

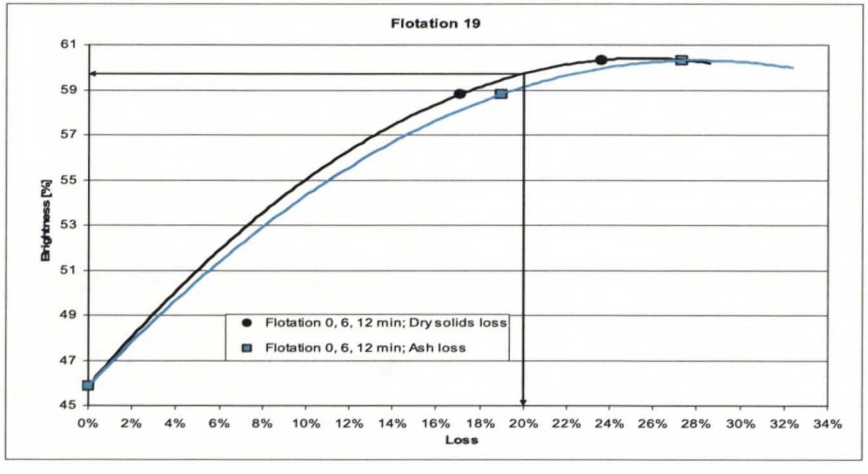

Flotation 14
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss


Flotation 15
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

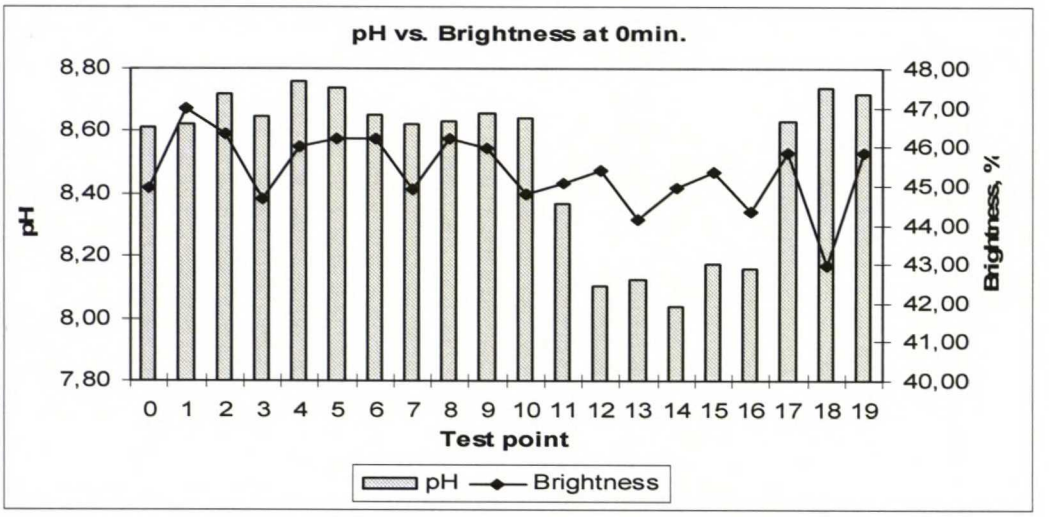

Flotation 16
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

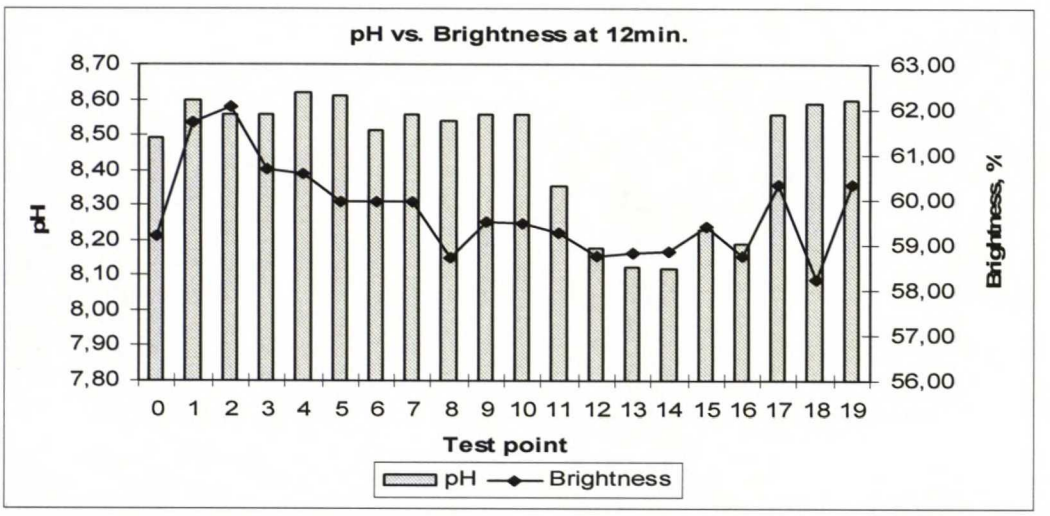

Flotation 17
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

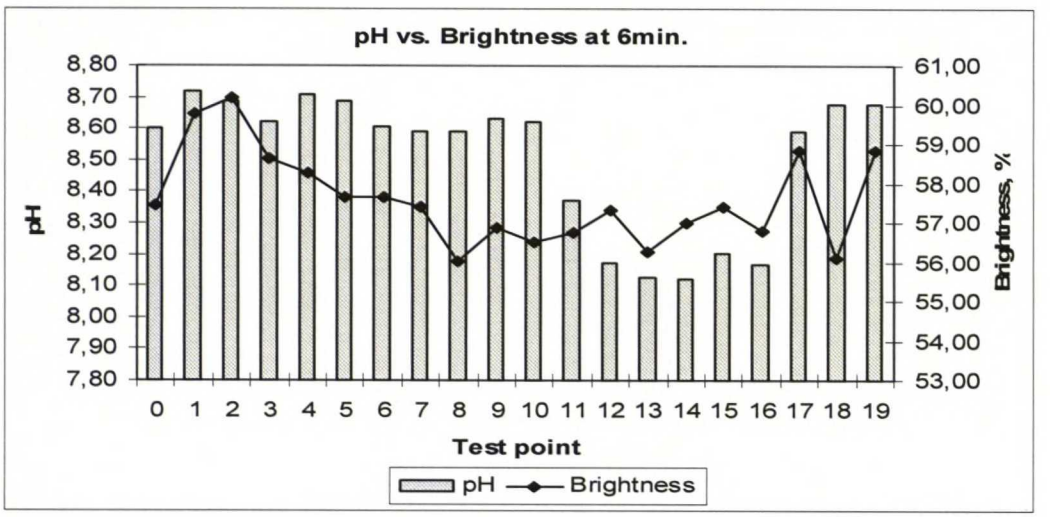

Flotation 18
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss


Flotation 19
Brightness [%]
Loss
Flotation 0, 6, 12 min; Dry solids loss
Flotation 0, 6, 12 min; Ash loss

Laboratory trial run, effect of pH to final brightness.



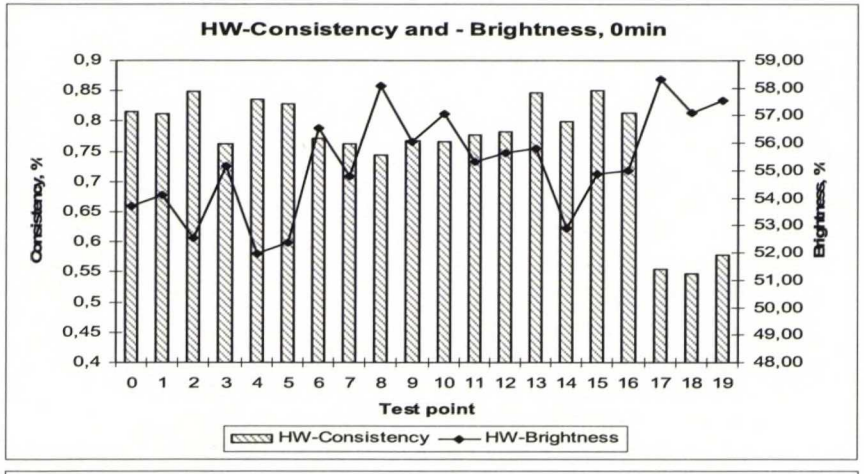


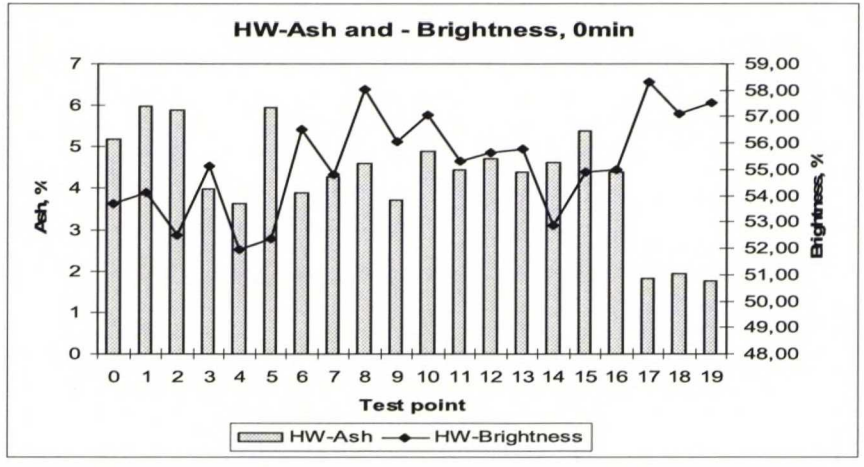


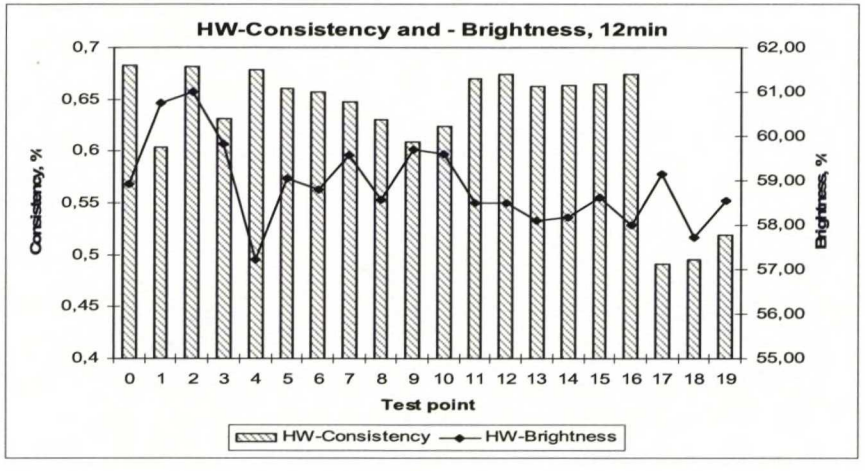
Results of the measurements made for fresh water.

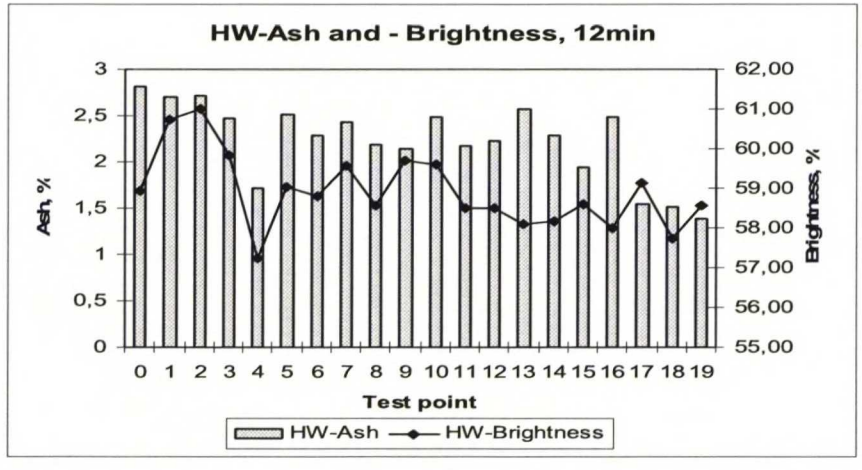
Fresh water		
Test point	°dH	pH
0	9,41	7,6
1	9,57	7,6
2	9,22	7,64
3	9,24	7,55
4	9,79	7,67
5	14,1	7,66
6	8,93	7,78
7	9,86	7,7
8	10,2	7,68
9	10,1	8,0
10	10	7,77
11	9,37	7,7
12	10,2	7,65
13	10,6	7,74
14	11,2	7,66
15	8,76	7,61
16	8,85	7,46
17	10,8	7,5
18	11,3	7,39
19	11,3	7,39

Dry solids content, ash content and brightness of the hyperwashed pulp of non-flotated pulp and after 12 min. flotation in laboratory trials.

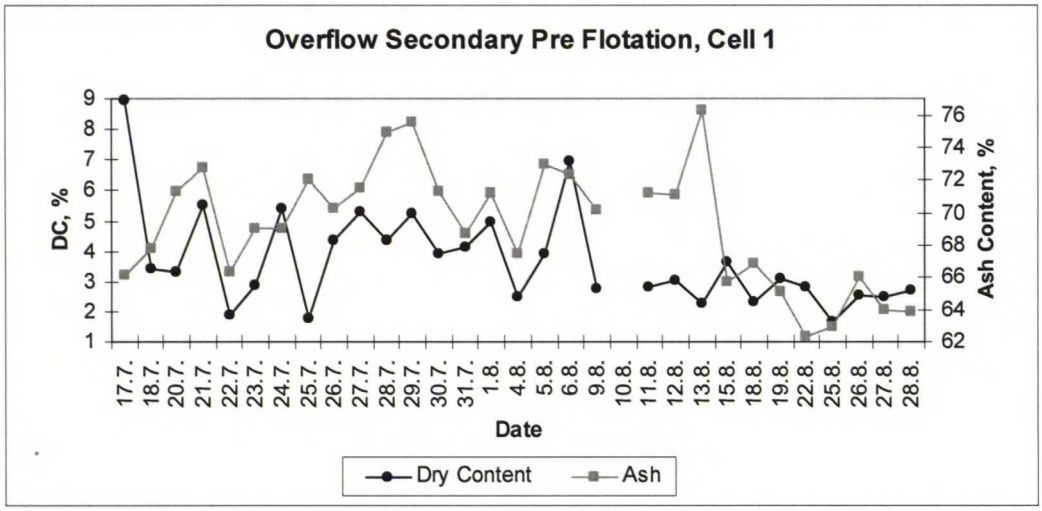


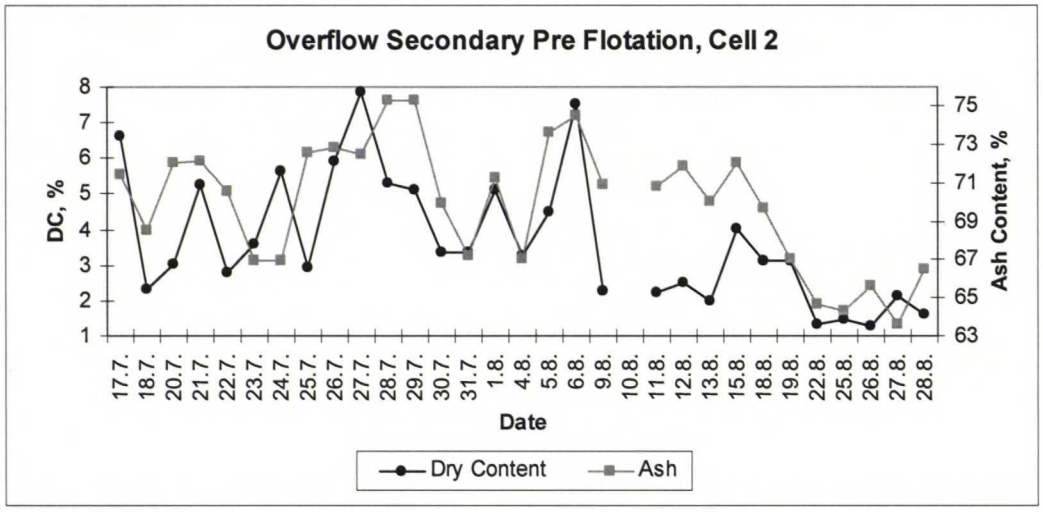


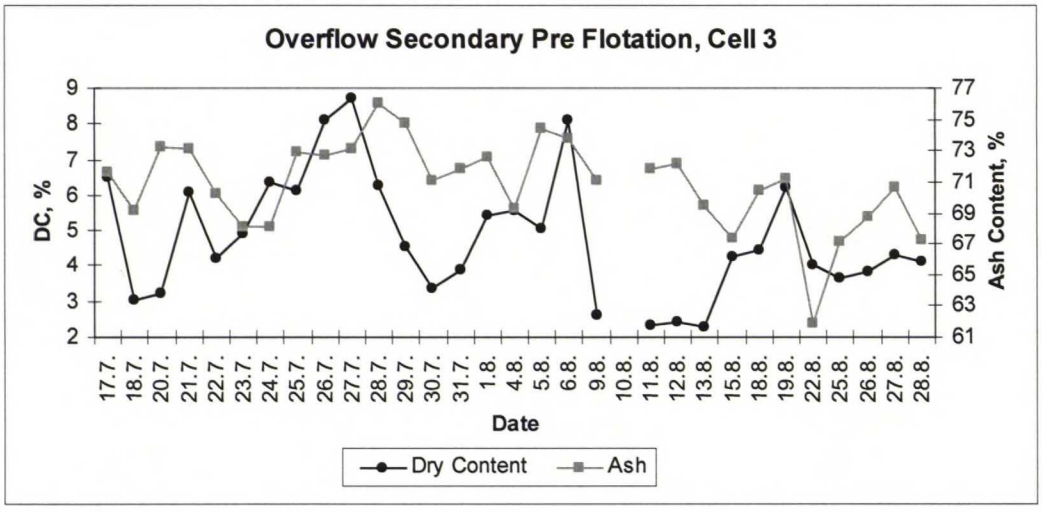




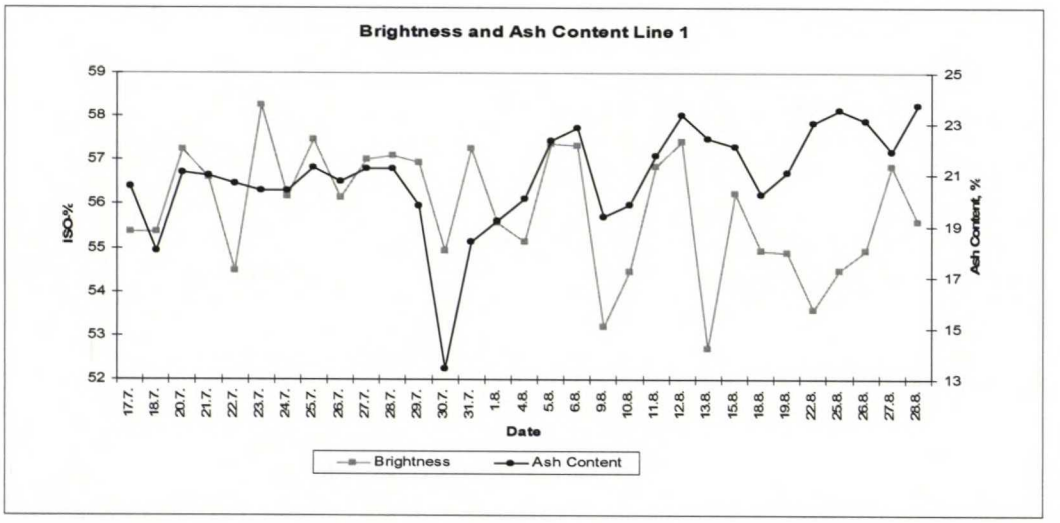
Dry solids and ash content of overflow form each secondary pre flotation cell in mill scale trial run.

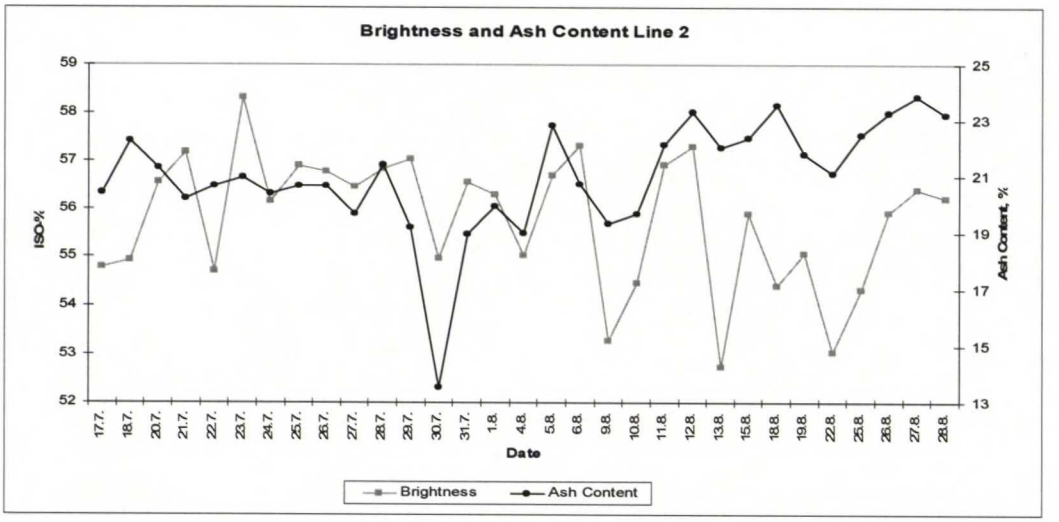


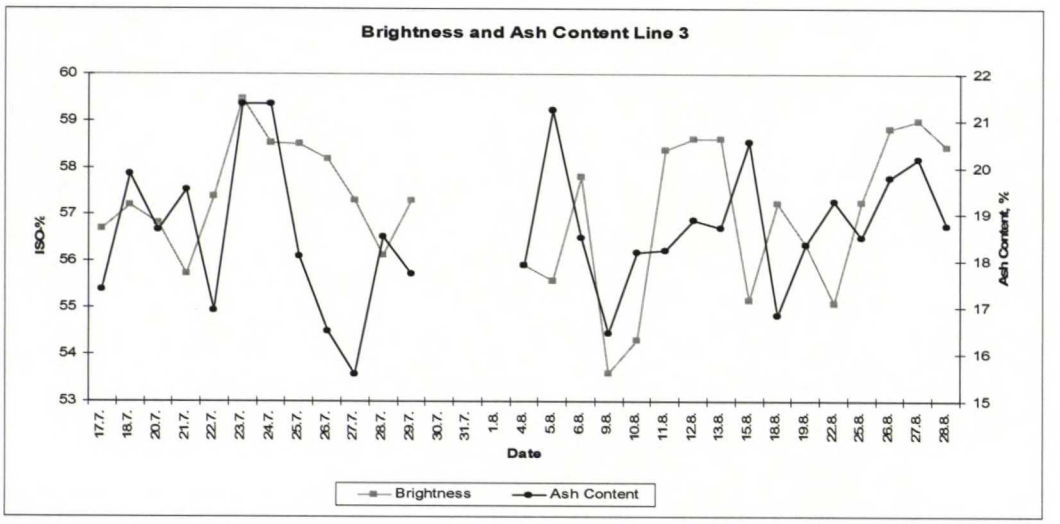




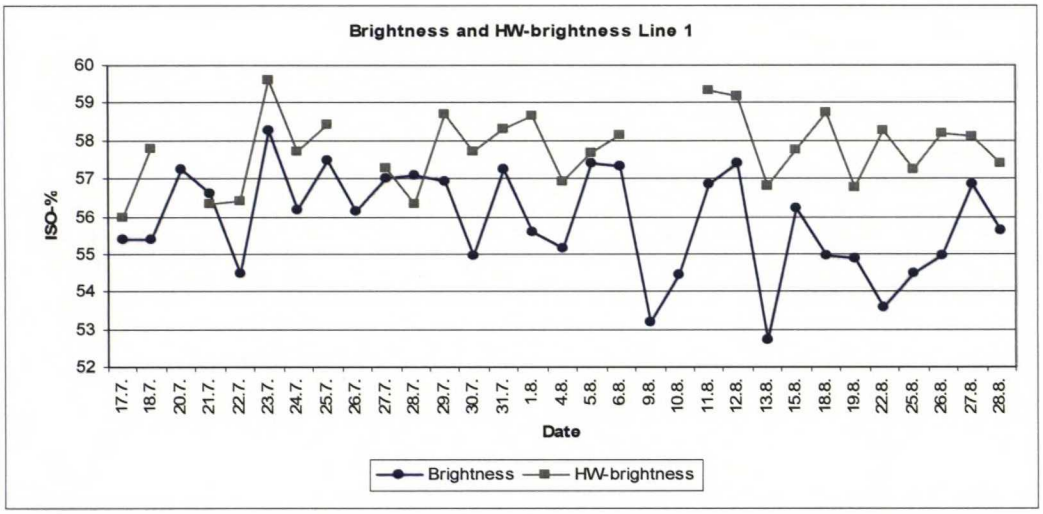
Brightness of the accept and its ash content for each pre flotation line in mill scale trial run.

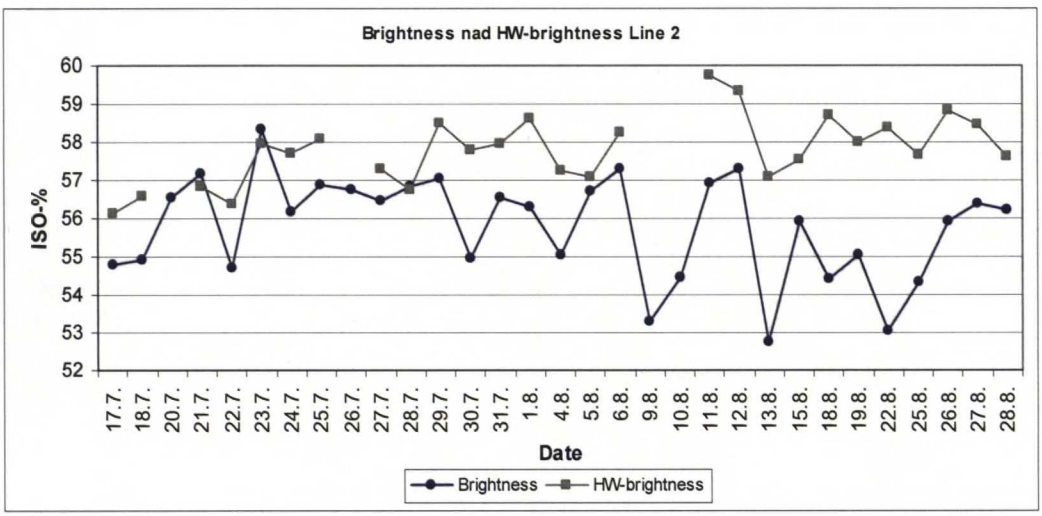


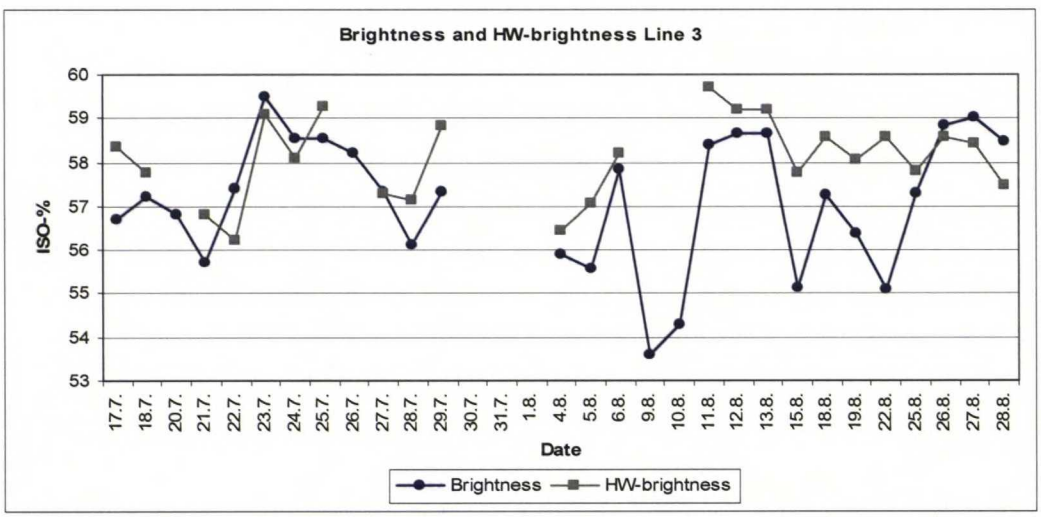




Brightness of the accept compared to hyperwashed brightness of each pre flotation line in mill scale trial run.







PKP-08